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National Surface Water Survey. National Stream Survey (Phase 1 - Pilot, Mid-Atlantic Phase 1 Southeast Screening, and Episodes Pilot) Quality Assurance Plan

Lockheed Engineering and Management
Services, Co., Inc., Las Vegas, NV

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NATIONAL SURFACE WATER SURVEY
NATIONAL STREAM SURVEY (PHASE I - PILOT, MID-ATLANTIC PHASE I, SOUTHEAST SCREENING, AND EPISODES PILOT)

QUALITY ASSURANCE PLAN

by

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16. ABSTRACT

This Quality Assurance plan documents the QA/QC and methods used for the National Stream Survey of the Aquatic Effects Research Program (Task Group E) of the National Acid Precipitation Assessment Program. The plan is based on the guidance and specifications provided by the Quality Assurance Management Staff (QAMS, 1980) of the Office of Research and Development. Methods are detailed in a companion document, but this plan gives the internal quality control used by the contract analytical laboratories.

Detailed QA/QC procedures are given for all processes from field sampling, through sample processing and analysis, to entry and verification of the data in a database. The data checks, statistical assessments and component comparisons used in data verification are presented in detail.

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ABSTRACT

The National Surface Water Survey of the National Acid Precipitation Assessment Program is a three-phase project to evaluate the current water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program to study future changes in aquatic resources. This manual describes the quality assurance plan for the first four field components of the National Stream Survey: the Phase I - Pilot Survey, the Phase I - Mid-Atlantic Survey, the Southeast Screening Survey, and the Episodes Pilot Survey.

To ensure that procedures are performed consistently and that the quality of the data generated can be determined, the Quality Assurance Project Plan for these four elements of the National Stream Survey specifies the following measures:

- Provide detailed, written sampling methodology.
- Simultaneously train all personnel participating in sampling and processing activities.
- Conduct site visits to each field operations base throughout the sampling period to ensure that all methods and quality assurance procedures are being performed properly.
- Perform extensive evaluation of analytical laboratories before their selection and throughout their participation.
- Assess variability introduced at each level of activity in mobile processing and analytical laboratories by utilizing audit samples (synthetic and natural lake samples), duplicates, and blanks along with routine samples.
- Provide detailed, written analytical methodology.
- Use internal quality control procedures at the analytical laboratory to detect potential contamination and to verify established detection limits.
- Enforce sample holding time requirements.
- Use quality control protocols in the field, at the mobile processing laboratory, and at the analytical laboratory to confirm that reported data are correct.

- Enter data into the data base twice, and scan for outlying values to detect and eliminate transcription errors.
- Verify data by means of range checks, internal consistency checks, and quality assurance evaluations.
- Validate verified data by analysis of the reasonableness of data, based on the values expected for the particular region or subregion involved.

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NATIONAL SURFACE WATER SURVEY
NATIONAL STREAM SURVEY (PHASE I - PILOT, MID-ATLANTIC PHASE I, SOUTHEAST SCREENING, AND EPISODES PILOT) QUALITY ASSURANCE PLAN

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1.0 INTRODUCTION

Data published in previous studies are consistent with the hypothesis that certain surface waters within the United States have decreased in pH, alkalinity, or both over time. Acidic deposition has been suggested as a contributor to such decreases. Also, numerous studies have led to the conclusion that the effects of acidic deposition on surface water chemistry are influenced by variations among associated lake, stream, and watershed characteristics (U.S. EPA, 1984a and 1984b). Attempts have been made to extrapolate local studies to the regional and national scale and thus to provide a quantitative estimate of the risk to aquatic resources (especially fish) from acidic deposition. These assessments have had only limited success because of problems associated with (1) the comparability of the sampling and analytical methodologies used in different studies, (2) the possibility of biased or nonrepresentative sampling sites, and (3) small and incomplete data bases.

The National Surface Water Survey (NSWS) of the National Acid Precipitation Assessment Program (NAPAP), Task Group E (Aquatic Effects) is designed to overcome some of these deficiencies. NSWS is a three-phase project to evaluate the present water chemistry of lakes and streams, determine the status of fisheries and other biotic resources, and select regionally representative surface waters for a long-term monitoring program to study future changes in aquatic resources.

Because of logistical and systematic differences between lakes and streams, NSWS was separated into lake and stream survey components. The first phase of the National Stream Survey (NSS) is a synoptic survey of the chemistry of streams and includes (1) a pilot survey in the southern Blue Ridge Province, (2) a full-scale survey in the Mid-Atlantic states, (3) a screening survey in the Southeast, and (4) an episodes pilot survey in the Mid-Atlantic states. This manual delineates the quality assurance (QA) plan for these four NSS components. A description of the project and its organization is given in the following sections.

The QA policy of the Environmental Protection Agency (EPA) requires that every monitoring and measurement project have a written and approved QA project plan (Costle, 1979a and 1979b). This requirement applies to all environmental monitoring and measurement efforts authorized or supported by EPA through regulations, grants, contracts, or other formal means. The QA project plan should specify the policies, organization, objectives, functional activities, QA activities, and quality control (QC) activities designed to achieve the data quality goals of the project. All project personnel should be familiar with the policies and objectives outlined in the QA project plan to ensure proper interaction of the sampling operations, laboratory operations, and data management.

EPA guidance states that the 16 items shown in Table 1.1 should be addressed in the QA project plan (U.S. EPA, 1980). Some of these items are extensively addressed in the analytical methods manual (Hillman et al., 1986) for this project; therefore, as allowed by the guidelines, method-specific discussions are not repeated in this document.

TABLE 1.1. SECTIONS IN THIS REPORT AND IN THE ANALYTICAL METHODS MANUAL THAT ADDRESS QUALITY ASSURANCE SUBJECTS

Subject	Section	
	This Report	Methods Manual
Title Page		
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2.0 PROJECT DESCRIPTION

Figure 2.1 shows the structure of NSWS as presently planned.

This document defines the QA requirements for four segments of NSS: (1) the Phase I - Pilot, a survey of approximately 60 streams; (2) the Mid-Atlantic Phase I, a survey of 250 streams; (3) the Southeast Screening, a survey of 200 streams; and (4) the Episodes Pilot, a study of the magnitude, frequency, duration, and causes of episodic events in streams. The following sections describe these four studies, delineate the objectives to be achieved by each study, and present the measures specified by the NSS QA project plan.

2.1 Components of the National Stream Survey

2.1.1 Phase I - Pilot Survey - The Phase I - Pilot Survey, which was conducted in the Southern Blue Ridge Province during spring 1985, had the following primary objectives:

- Test the statistical sampling design.
- Test all methods that will be used during the survey.
- Finalize the data quality objectives (DQOs) for Phase I.
- Finalize the QA/QC guidelines for Phase I.
- Train personnel for the field operations.
- Test the data analysis plan.

The Phase I - Pilot Survey is described in detail in Messer et al., 1986.

2.1.2 Mid-Atlantic Phase I Survey - The Mid-Atlantic Phase I Survey involves sampling approximately 250 stream reaches in an area bounded by the Catskill and Pocono Mountains to the north, the North Carolina-Virginia state line to the south, the approximate western boundaries of Pennsylvania and West Virginia to the west, and the Atlantic Ocean. This region is expected to contain many areas of low acid-neutralizing capacity (ANC) waters, and it is subject to relatively high levels of acidic deposition. Each stream reach is sampled twice during spring baseflow conditions, at its upstream and its downstream nodes.

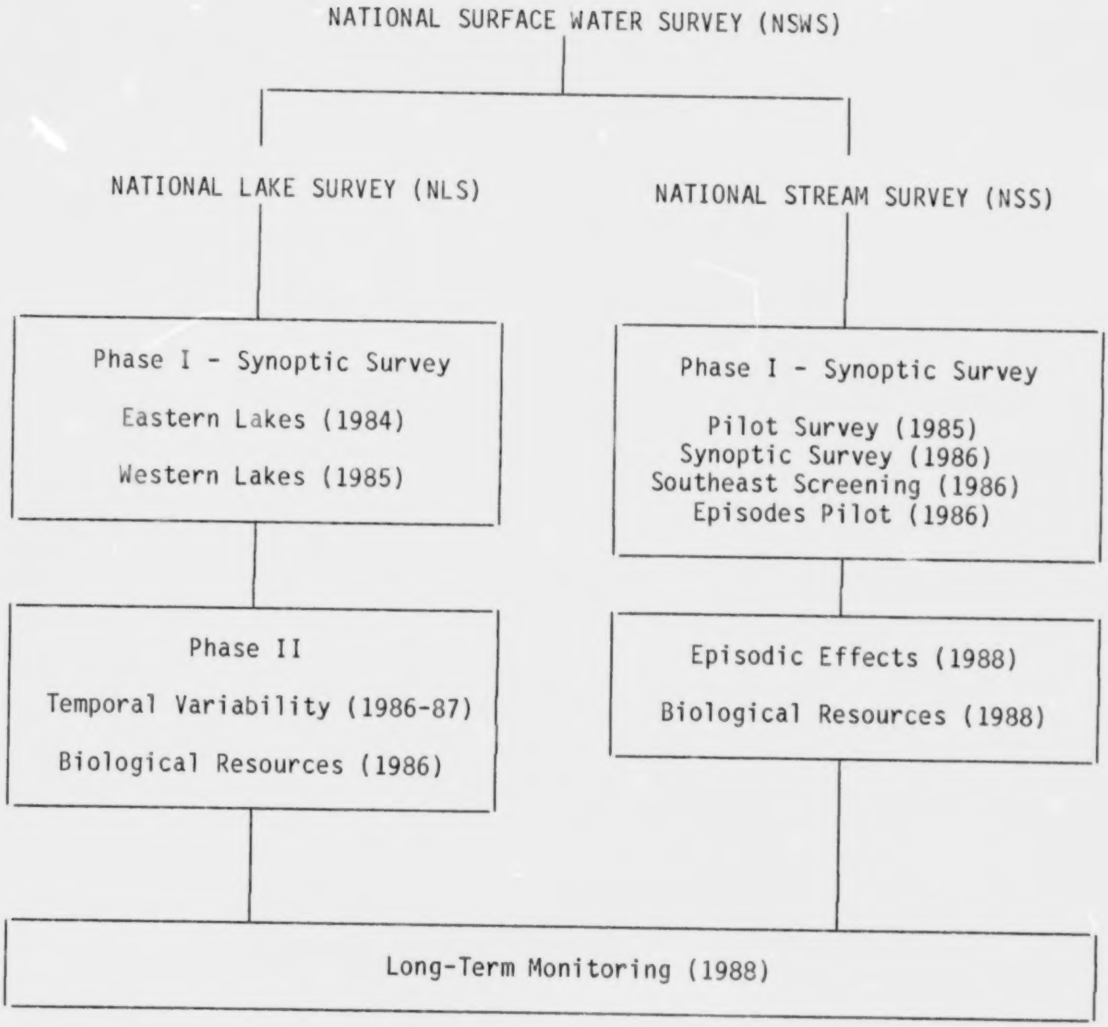

NATIONAL SURFACE WATER SURVEY (NSWS)
NATIONAL LAKE SURVEY (NLS)
NATIONAL STREAM SURVEY (NSS)
Phase I - Synoptic Survey
Eastern Lakes (1984)
Western Lakes (1985)
Phase I - Synoptic Survey
Pilot Survey (1985)
Synoptic Survey (1986)
Southeast Screening (1986)
Episodes Pilot (1986)
Phase II
Temporal Variability (1986-87)
Biological Resources (1986)
Episodic Effects (1988)
Biological Resources (1988)
Long-Term Monitoring (1988)

Figure 2.1. Organization of the National Surface Water Survey.

The primary objectives of the Mid-Atlantic Phase I survey are those of the overall NSS-Phase I:

- Determine the percentage, extent (miles, drainage area), and location of streams that are in potentially acid-sensitive regions of the United States and that are presently acidic.

- Determine the percentage, extent, and location of such streams that are presently characterized by low alkalinity and that may become acidic in the future.

- Determine which streams are representative of typical subpopulations of streams in a particular region and from these identify which streams should be more intensively studied.

2.1.3 Southeast Screening Survey - It is necessary to decide whether and where to extend Phase I sampling. The National Lake Survey will be useful in targeting potential areas of interest in the Northeast, Midwest, and West. However, virtually no data are available for the southeastern states other than historical data depicted on the regional alkalinity maps and from the Phase I - Pilot Survey.

The purpose of the Southeast Screening Survey is to prioritize other potential NSS regions in the Southeast for full Phase I study. The statistical design will allow regional characterization, just as in the Phase I study area. However, each stream is sampled only once (at two sites); thus, no temporal variance estimate will be available. The single sample is not expected to provide enough information to allow robust classification of the Phase I streams for later study. Also only crude discharge estimates are made in the screening area, and streams are sampled only under baseflow conditions.

The screening area comprises the Southern Appalachian Mountains (exclusive of the Phase I - Pilot Survey area), the Piedmont, the Ouachita and Ozark Mountains, and parts of Florida. Approximately 400 samples will be collected from the screening area from upstream and downstream nodes on each of 200 streams.

The primary objectives of the Southeast Screening Survey are the same as the objectives of the Mid-Atlantic Phase I Survey and of NSS-Phase I, given in section 2.1.2.

2.1.4 Episodes Pilot Survey - The Episodic Response Project (of NAPAP Task Group E3) has as its primary objective predicting the magnitude, frequency, duration, and causes of episodic events in lakes and streams. These events cause marked shifts from baseflow conditions in pH and associated parameters. In areas dominated by snowpack, such episodes result from snowmelt, often exacerbated by warm days or rainfall. In warmer regions, episodes are usually associated with rain events. The field work described here represents a pilot effort aimed at providing a preliminary assessment of the frequency, duration, and causes of such episodes in the Mid-Atlantic states. It also is expected to provide sufficient information about design and logistics aspects to allow a cost-effective, full-scale, regional episodes survey (or surveys) to be implemented.

There are several ways to estimate the number and frequency of episodes, and each method has its own set of conceptual and logistical difficulties. A pilot survey is valuable because it helps answer questions about survey design. Thus, a pilot survey helps produce an efficient design for a full-scale episodic effects field effort. It is anticipated that approximately five stormfronts will be suitable for event sampling during the stream survey. Six episode teams will sample each event, so 30 sets of event data should be obtained. Each team will collect 4 samples per event under ideal conditions; thus, approximately 120 samples should be collected for the Episodes Pilot Survey. In addition to collection of water samples, pH, specific conductance, and dissolved oxygen concentration will be determined at 30-minute intervals throughout each event.

2.2 Data Quality Objectives

DQOs, in terms of anticipated value range, detection limits, and precision, were defined for each measurement parameter in early 1985. These QA goals were originally based on published literature, statistical error propagation, and Eastern Lake Survey findings. Equipment, sampling protocols, and analytical methodologies were selected and standardized in order to achieve the DQOs. The Phase I - Pilot Survey provided the opportunity to evaluate and revise methodologies, equipment, and DQOs. The observed range of values from the Phase I - Pilot Survey, required detection limits, and relative intralaboratory precision goals for each variable are summarized in Table 4.1.

2.3 Specifications of the Quality Assurance Project Plan

To ensure that procedures are performed consistently and that the quality of the data generated can be determined, the QA project plan for NSS specifies the following measures:

- Provide detailed, written sampling methodology (protocols are documented in Hagley et al., 1986).

- Simultaneously train all personnel who will participate in field activities.

- Conduct site visits to each field operations base throughout the sampling period to ensure that all methods are being performed properly.

- Perform extensive evaluation of analytical laboratories before their selection and throughout their participation.

- Assess variability introduced at each level of activity in the mobile processing and analytical laboratories by preparing (if necessary) and analyzing audit samples (synthetic samples and natural lake samples), duplicates, and blanks along with routine samples.

  NOTE: "Mobile processing laboratory" refers to the laboratory complex of trailers located in Las Vegas, Nevada, where sample processing and preliminary analyses are performed. For the Phase I - Pilot Survey, the mobile laboratory was located in the field. "Analytical laboratory" refers to the off-site contract laboratory that performs the more sophisticated analyses.

- Provide detailed, written analytical methodology (Hillman et al., 1986).

- Use internal QC procedures at the analytical laboratory to detect potential contamination and to verify established detection limits.

- Enforce holding time requirements.

- Use protocols in the field, in the mobile processing laboratory, and in the analytical laboratories to confirm that reported data are correct.

- Enter data into the data base twice, and scan for outlying values to detect and eliminate transcription errors.

- Verify data by means of range checks, internal consistency checks, and QA evaluations.

- Validate verified data by analyzing the reasonableness of data; base the analysis on the values expected for the particular region or subregion involved.

3.0 PROJECT ORGANIZATION

Figure 3.1 illustrates the NSWS management structure. The program director is the EPA official who has overall responsibility for the program. The responsibilities of the program manager, technical director, and administrative coordinator are as follows:

Program Manager

The program manager is the EPA Headquarters representative for NSWS and serves as the liaison among the headquarters staff, the laboratory directors, and NAPAP. Questions regarding general management and resources should be forwarded to the program manager through the technical director.

Technical Director

The technical director performs program responsibilities at the discretion of the program manager. The primary role is to see that the program objectives are satisfied, that the components of the program are well-integrated, and that deadlines are met. The technical director coordinates and integrates the activities of the Environmental Research Laboratory at Corvallis, Oregon (ERL-C), the Environmental Monitoring Systems Laboratory at Las Vegas, Nevada (EMSL-LV), and the Oak Ridge National Laboratory (ORNL) at Oak Ridge, Tennessee. The technical director also coordinates peer review and resolves issues of responsibility. The office is the focal point of general public inquiry and distribution of report information. The technical director represents the program manager as necessary and keeps the program manager informed of EPA laboratory activities, progress, and performance.

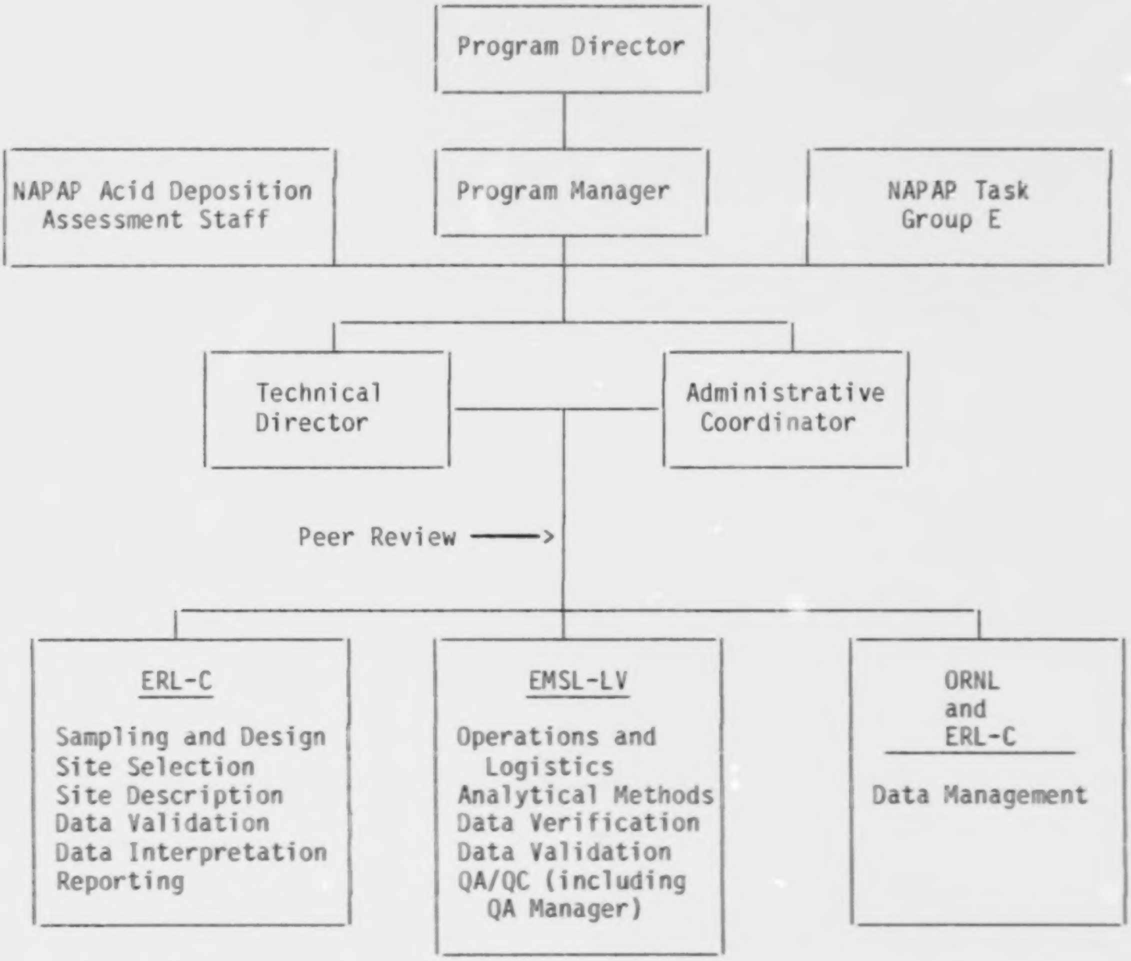
Administrative Coordinator

The administrative coordinator reports directly to the program manager. The primary role of this position is to monitor the budget and personnel needs of the survey staff. The administrative coordinator also makes contractual arrangements at the headquarters level and provides special services as needed.

The roles of the laboratories are as follows:

Environmental Research Laboratory, Corvallis

In view of the role the Corvallis laboratory plays in the Agency's acidic deposition research program and the major roles it must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NAPAP Task Group E
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Peer Review
ERL-C
Sampling and Design
Site Selection
Site Description
Data Validation
Data Interpretation
Reporting
EMSL-LV
Operations and Logistics
Analytical Methods
Data Verification
Data Validation
QA/QC (including QA Manager)
ORNL and ERL-C
Data Management

Figure 3.1. National Surface Water Survey internal management structure.

perform during the survey program, it is appropriate that ERL-C becomes a primary focal point for NSS. Its responsibilities for all phases of NSWS include:

- developing the sampling design
- selecting the sampling sites
- preparing sampling protocols (jointly with EMSL-LV)
- collecting supplemental historical and other available data on each sampling site (aquatic and terrestrial components)
- analyzing data (jointly with EMSL-LV)
- interpreting data and maps
- preparing reports (final and progress reports, with contributions from the other laboratories relative to their responsibilities)
- assessing and resolving all science-related issues other than QA/QC and data management (jointly with other laboratories as necessary)
- coordinating survey activities with NAPAP management staff.

Environmental Monitoring Systems Laboratory, Las Vegas

The Las Vegas laboratory has particular expertise in matters relating to QA/QC, logistics, analytical services, and sampling protocols. The responsibilities of this laboratory, for all phases of NSWS, include:

- developing QA/QC procedures for all components of the program except data management (ORNL and ERL-C)
- preparing all sampling protocols (jointly with ERL-C)
- preparing the analytical methods manual
- preparing the field training and operations manual
- preparing the mobile processing laboratory operations manual for those component surveys for which such information is not included in the other manuals.
- preparing and implementing the QA project plan

- coordinating logistical support and equipment needs for all field operations
- training sampling personnel
- distributing all samples to analytical laboratories
- developing and implementing QA/QC procedures for verifying all field measurements and analytical laboratory data
- independently assessing field measurements and laboratory data quality (bias and variability)
- assessing and resolving all problems pertaining to QA/QC, logistics, and analytical services.

Oak Ridge National Laboratory

ORNL has considerable expertise in managing large data bases, manipulating data, and restructuring data bases to satisfy data analysis needs. ERL-C oversees the activities of ORNL, which has NSWS responsibilities for:

- developing and maintaining a data management system
- entering all field, laboratory, and support data into the data base, and simultaneously assuring data quality
- preparing computer-generated summary tables, statistics, and graphics for reports.

4.0 QUALITY ASSURANCE OBJECTIVES FOR PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY

4.1 Precision and Accuracy

The QA objectives for precision and accuracy of the parameters being measured are given in Table 4.1. Precision and accuracy are determined in part by analyzing data from QA/QC samples. QA samples include the following:

- Field blank - A field blank is a deionized water sample that meets specifications for ASTM Type 1 reagent water (ASTM, 1984). The blank sample is carried to the stream and is processed through the sampling device as though it were a routine sample. One field blank is collected for each sampling region on each operating day. Field blank data are used to establish the estimated system decision limit (the lowest instrument signal that can be distinguished from the background), the quantitation limit (the lowest concentration of an analyte that can be measured with reasonable precision), and the system detection limit (the lowest concentration that can be measured above the system decision limit) that can be expected for each type of analysis. For data interpretation, a data point for a field blank above the expected value is considered a positive response.

- Field duplicate - A field duplicate is a second sample collected at the stream site by the same team immediately after the routine sample is collected. Field duplicate data are used to estimate the overall within-batch precision for the sampling and analysis process. One field duplicate is collected per field base per operating day.

- Audit samples - Audit samples are materials with known characteristics, used to determine the accuracy of the measurement system. Two types of audit samples serve as QA checks for NSS: field audit samples (natural and synthetic) help to check the overall field and laboratory performance; laboratory audit samples (natural and synthetic) help to check the performance of the analytical laboratory. Audit samples are discussed in Section 10.0.

- Trailer duplicates; trailer blanks - Trailer duplicates and trailer blanks are used to check the precision of mobile processing laboratory measurements.

Field QA/QC samples are used primarily by the sampling teams and mobile processing laboratory staff to check the accuracy of the measurement

TABLE 4.1. DATA QUALITY OBJECTIVES[a] FOR PRECISION, ACCURACY, AND DETECTABILITY

Parameter[b]	Units	Observed Range[c]	Required Detection Limits	Precision Relative Standard Deviation (RSD) Upper Limit (%)[d]	Accuracy Maximum Absolute Bias (%)
Al, Total extractable	mg/L	0.0-0.3	0.005	10 (if conc. >0.01 mg/L) 20 (if conc. ≤0.01 mg/L)	10/20
Al, Total	mg/L	0.005-75	0.005	10 (if conc. ≥0.01 mg/L) 20 (if conc. ≤0.01 mg/L)	10/20
Al, Non-exchangeable and total PCV reactive	mg/L	---	0.010	10 (if conc. >0.01 mg/L) 20 (if conc. ≤0.01 mg/L)	10/20
ANC	μeq/L	-8-3,000	e	10	10
BNC	μeq/L	0.0-400	e	10	10
Ca	mg/L	0.3-50	0.01	5	10
Cl^-	mg/L	0.3-30	0.01	5	10
True Color	PCU[f]	0-750	0	±5[g]	--
DIC	mg/L	0.1-30	0.05	10	10
DO	mg/L	7.1-12.1	---	5	5
DOC	mg/L	0.1-8	0.1	5 (if conc. >5 mg/L) 10 (if conc. ≤5 mg/L)	10
F^-, Total dissolved	mg/L	0.0-0.2	0.005	5	10
Fe	mg/L	0.0-0.6	0.01	10	10
K	mg/L	0.2-5	0.01	5	10

(continued)

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[a] The objective for completeness of data is 90 percent or better for all parameters.

[b] Dissolved ions and metals are being determined, except where noted.

[c] Range of values observed in stream waters during Phase I - Pilot Survey.

[d] Unless otherwise noted, this is the RSD at concentrations greater than (10 times) the instrumental detection limits.

[e] Absolute blank value must be ≤ 10 μeq/L.

[f] PCU = platinum-cobalt units.

[g] Absolute precision/accuracy goal in terms of applicable units.

TABLE 4.1. (Continued)

Parameter[b]	Units	Observed Range[c]	Required Detection Limits	Precision Relative Standard Deviation (RSD) Upper Limit (%)[d]	Accuracy Maximum Absolute Bias (%)
Mg	mg/L	0.2-15	0.01	5	10
Mn	mg/L	0.0-0.2	0.01	10	10
Na	mg/L	0.4-22	0.01	5	10
NH_4^+	mg/L	0.0-0.4	0.01	5	10
NO_3^-	mg/L	0.0-9	0.005	10	10
pH, Field	pH units	5-8.5	---	±0.1 pH[g]	±0.1 pH[g]
pH, Analytical lab	pH units	5-8.5	---	±0.05 pH[g]	±0.1 pH[g]
P, Total dissolved[h]	mg/L	0.002-1.5	0.002	10 (if conc. >0.01 mg/L) 20 (if conc. <0.01 mg/L)	10 20
SiO_2	mg/L	3-25	0.05	5	10
SO_4^{2-}	mg/L	0.3-20	0.05	5	10
Specific Conductance	µS/cm	7-300	[i]	2	5
Turbidity	NTU	0.1-1,800	2	10	10

[b] Dissolved ions and metals are being determined, except where noted.

[c] Range of values observed in stream waters during pilot study.

[d] Unless otherwise noted, this is the RSD at concentrations above (about 10 times) instrumental detection limits.

[g] Absolute precision/accuracy goal in terms of applicable units.

[h] For the Phase I - Pilot Survey, total P is determined (samples were unfiltered). For the Mid-Atlantic Phase I, Southeast Screening, and Episodes Pilot Surveys, total dissolved P is determined (samples are filtered).

[i] The mean of six nonconsecutive blank measurements must not exceed 0.9 µS/cm.

system in the field. Field QA/QC samples include trailer duplicates, trailer (calibration) blanks, quality control check samples (QCCSs) for pH and specific conductance at the site, and mobile processing laboratory QCCSs (for pH, DIC, and turbidity). These samples are described in Sections 6 and 7.

Analytical laboratory QA/QC samples include calibration blanks, reagent blanks, analytical laboratory duplicates, QCCSs, and detection limit QCCSs. These are described in Section 9.0.

4.2 Completeness

The objective for completeness of data (the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under correct normal conditions) is 90 percent or better for all parameters. This figure is based on experience gained during previous studies and is subject to change during the survey.

4.3 Representativeness

The question of representativeness is an important one. NSS is designed to achieve the objectives outlined in Section 2. It is not intended to determine the chemistry of any given reach in detail but to obtain a good index of stream chemistry for each reach, so that reaches can be classified correctly. Therefore, achieving survey objectives does not require that the samples taken from a reach be completely representative of those waters. Only two samples from each of two sites per reach (the upstream and downstream nodes) are taken during the Mid-Atlantic Phase I Survey. For the Episodes Pilot Survey, a sample is taken at the downstream node during each of the following episode hydrologic stages: baseflow, rising, peak, and falling. For the Southeast Screening Survey, each reach is sampled only once at the upstream node and once at the downstream node. However, a determination of whether this level of sampling is sufficient to achieve the objectives of Phase I can be made only when estimates of "within reach" and "among reach" variances are obtained. Estimates of these variances will be made using currently available data and the statistical sampling design for Phase I, which will be modified if necessary (see Section 5). In later NSS phases, more intensive studies of individual reaches will be performed.

4.4 Comparability

Comparability is assured by having a uniform set of procedures for all sampling teams and a uniform set of units for reporting the data. Furthermore, the QA procedures described in succeeding sections allow for the determination of bias for each sampling team and analytical laboratory so that their results can be compared.

5.0 SAMPLING STRATEGY

This section provides a summary of the sampling design. More complete discussions are presented in the draft research plan (U.S. EPA, 1985) and in the draft sampling plan (Overton, 1985).

5.1 Selection of Subregions for Sampling

The first process in designing the sampling strategy is to determine what geographic regions and subregions are to be sampled. Highest priority was given to regions in which a majority of surface waters were expected to have low ANC based on current EPA alkalinity maps (Omernik and Powers, 1983).

The Phase I - Pilot Survey was conducted in subregion 2A(S) - the Southern Blue Ridge Province.

The subregions selected for the Mid-Atlantic Phase I Survey are the following (see Figure 5.1.):

- the Pocono and Catskill Mountains (1D)
- the Pine Barrens and Chesapeake Bay (3B)
- the northern portion of the Valley and Ridge Province (2B(N))
- the northern portion of the Appalachian Plateau (2C(N)).

Four stream populations are targeted for the Southeastern Screening Survey:

- the Piedmont (3A)
- the Ozark and Ouachita Mountains (2D)
- the coastal plain in Florida (3C)
- the Southern Appalachian Plateau (2A(N), 2B(S), and 2C(S)).

Subregions selected for sampling during the Episodes Pilot Survey are the same as those selected for the Mid-Atlantic Phase I Survey.

5.2 Selection of Reaches for Potential Sampling (First Stage Sample)

The stream population of interest drains watersheds of several tenths to tens of square miles (10^2 to 10^4 ha) with a maximum of 60 square miles (1.55×10^4 ha).

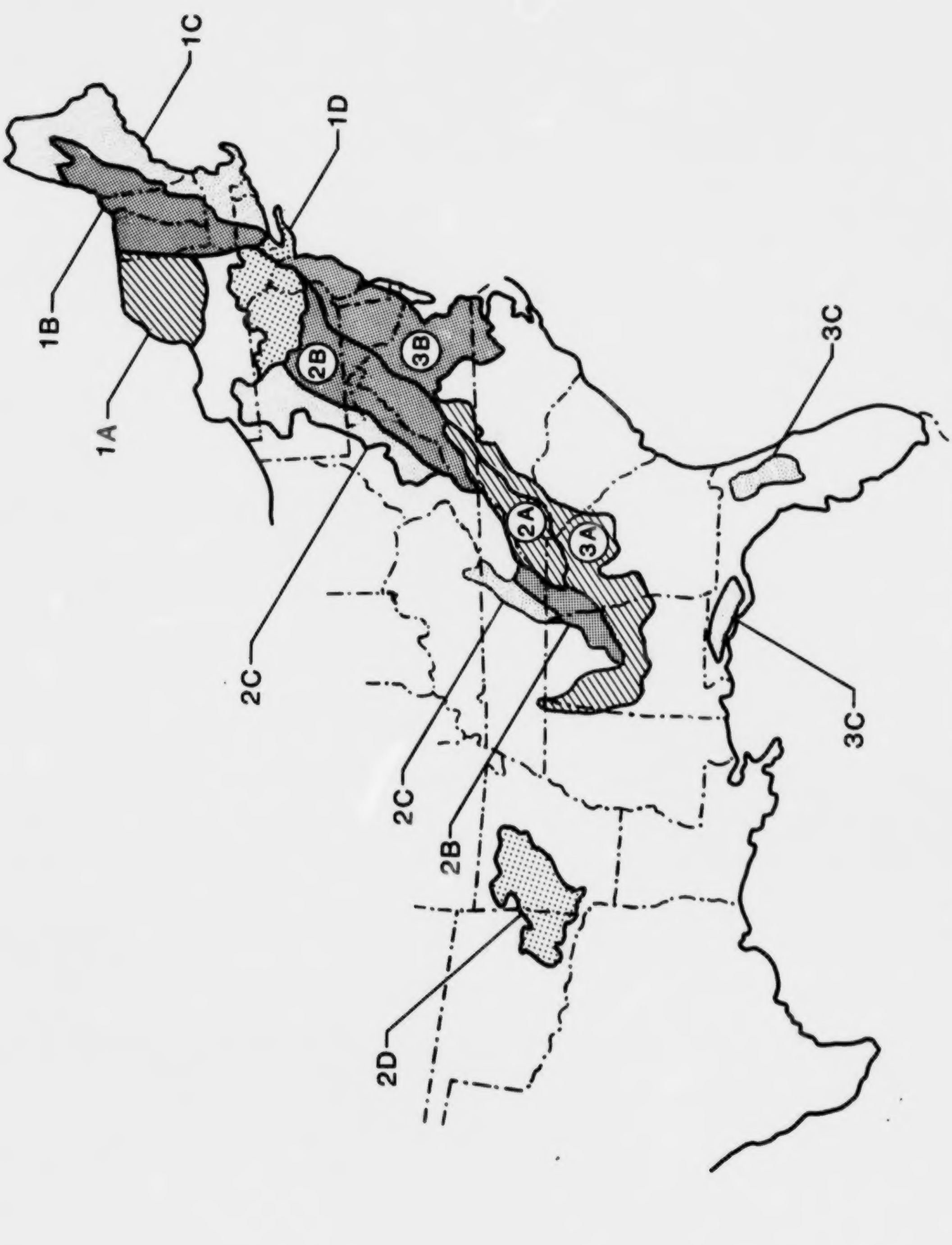

1A
1B
1C
1D
2A
2B
2C
2D
3A
3B
3C

Figure 5.1. National Stream Survey subregions. Areas targeted for sampling in 1986 are stippled.

A point-frame sampling design is used to select reaches for possible sampling (see Figure 5.2). A reach is defined as a blue-line stream (as indicated on a 1:250,000-scale topographic map) that lies between the confluences of two tributaries. The point frame is a rectangular grid of dots on an acetate transparency that is placed at random on a 1:250,000-scale topographic map. A reach is included in the first stage sample if it is intersected by a line drawn perpendicular to the elevation contours, proceeding from a grid point in a downslope direction (Figure 5.2). This sampling design produces a probability sample of reaches with an expected frequency of inclusion proportional to the direct drainage area, a_1, of each reach. Boundary and reservoir reaches, large rivers, tidal reaches, urban drainages, and severely polluted reaches (e.g., reaches dominated by acid mine drainage or fossil fuel brines) are excluded from the base of reaches for possible sampling. These reaches were excluded using low pH (less than 3.3) or high conductance (greater than 500 µS/cm for inland areas and greater than 250 µS/cm for tidal areas) as criteria.

5.3 Selection of Sampling Sites (Second Stage Sample)

The next task is to select a subpopulation of the first stage sample upon which to make physical measurements. A sample size of 50 per stratum has proven to be useful in earlier components of NSWS. To achieve a more homogeneous inclusion probability, the selections are weighted with a conditional inclusion probability inversely proportional to the area of direct watershed. An additional stratum of reaches with ANC less than 50 µeq/L is also included in the survey, and 29 "special interest" reaches will be sampled. These reaches include selected sites in the ongoing long-term monitoring project of NAPAP Task Group E, in which storm events will also be monitored, as well as other intensively studied watersheds in the area. Second stage sampling sites for the Phase I - Pilot Survey are shown in Figure 5.3, those for the Mid-Atlantic Phase I Survey are shown in Figure 5.4, and those for the Southeast Screening Survey are shown in Figures 5.5, 5.6, and 5.7.

5.4 Selection of Types and Locations of Measurements

The third stage sampling design involves the designation of what physical and chemical measurements should be taken on each second stage reach, and when and where to take them in order to best characterize the reach. Table 5.1 lists the parameters that will be measured for all NSS samples.

A point sample at the downstream node may not represent the chemistry of the reach lying above it. Within-reach chemistry may change along the reach as a result of instream processes (e.g., primary productivity), contributions from other streams that do not appear on 1:250,000-scale

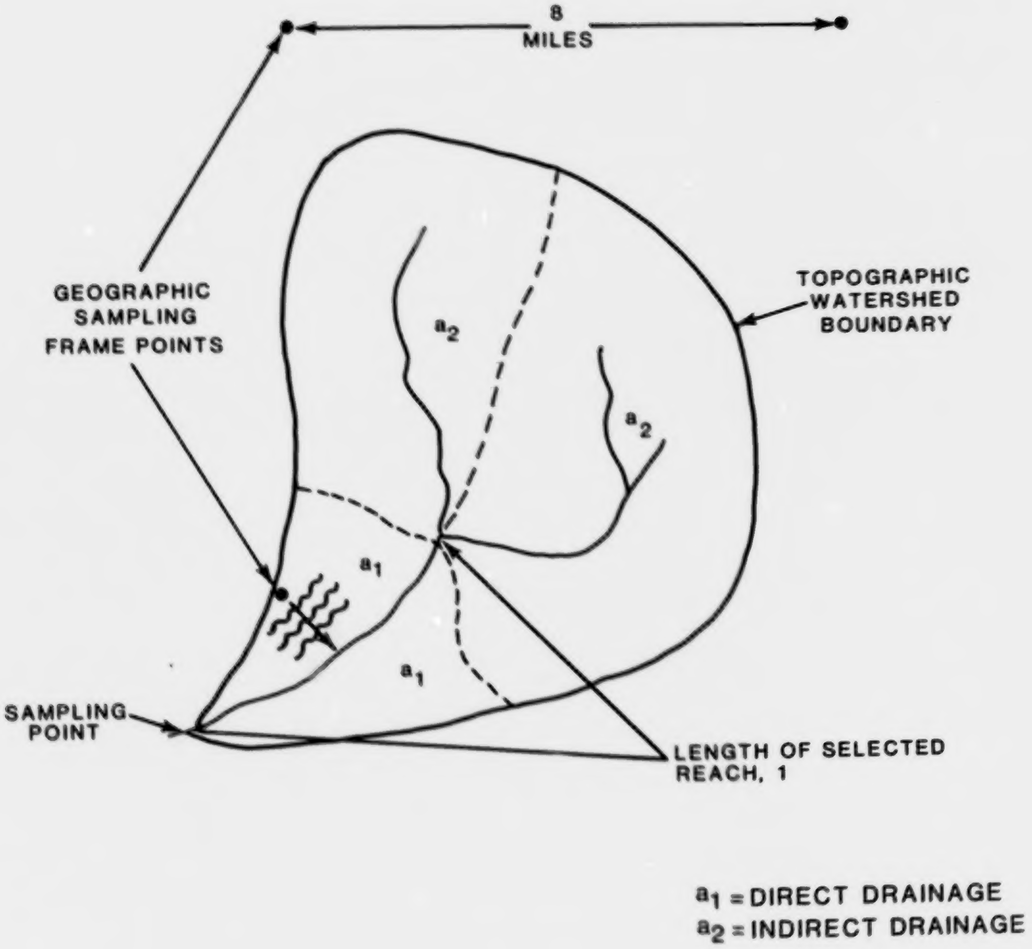

8
MILES
GEOGRAPHIC
SAMPLING
FRAME POINTS
TOPOGRAPHIC
WATERSHED
BOUNDARY
a2
a2
a1
a1
SAMPLING
POINT
LENGTH OF SELECTED
REACH, 1
a1 = DIRECT DRAINAGE
a2 = INDIRECT DRAINAGE

Figure 5.2. Description of sampling procedure for National Stream Survey study reaches. The sampling-frame points correspond to a uniform geographic grid. The lower left point results in inclusion of the watershed shown, provided $a_1 + a_2$ is less than 60 mi^2 (1.55×10^4 ha).

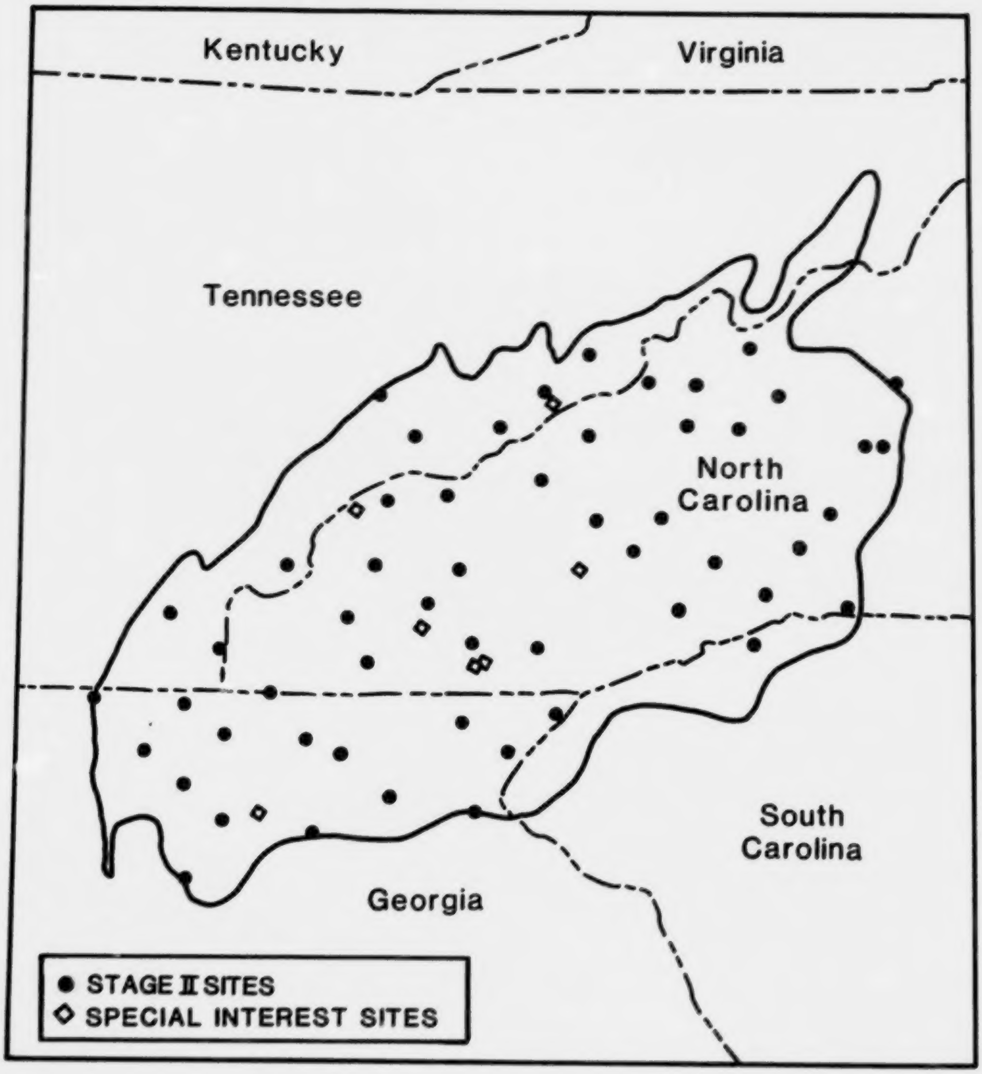

Kentucky
Virginia
Tennessee
North Carolina
South Carolina
Georgia
● STAGE II SITES
◇ SPECIAL INTEREST SITES

Figure 5.3. National Stream Survey Phase I - Pilot Survey second stage sampling sites.

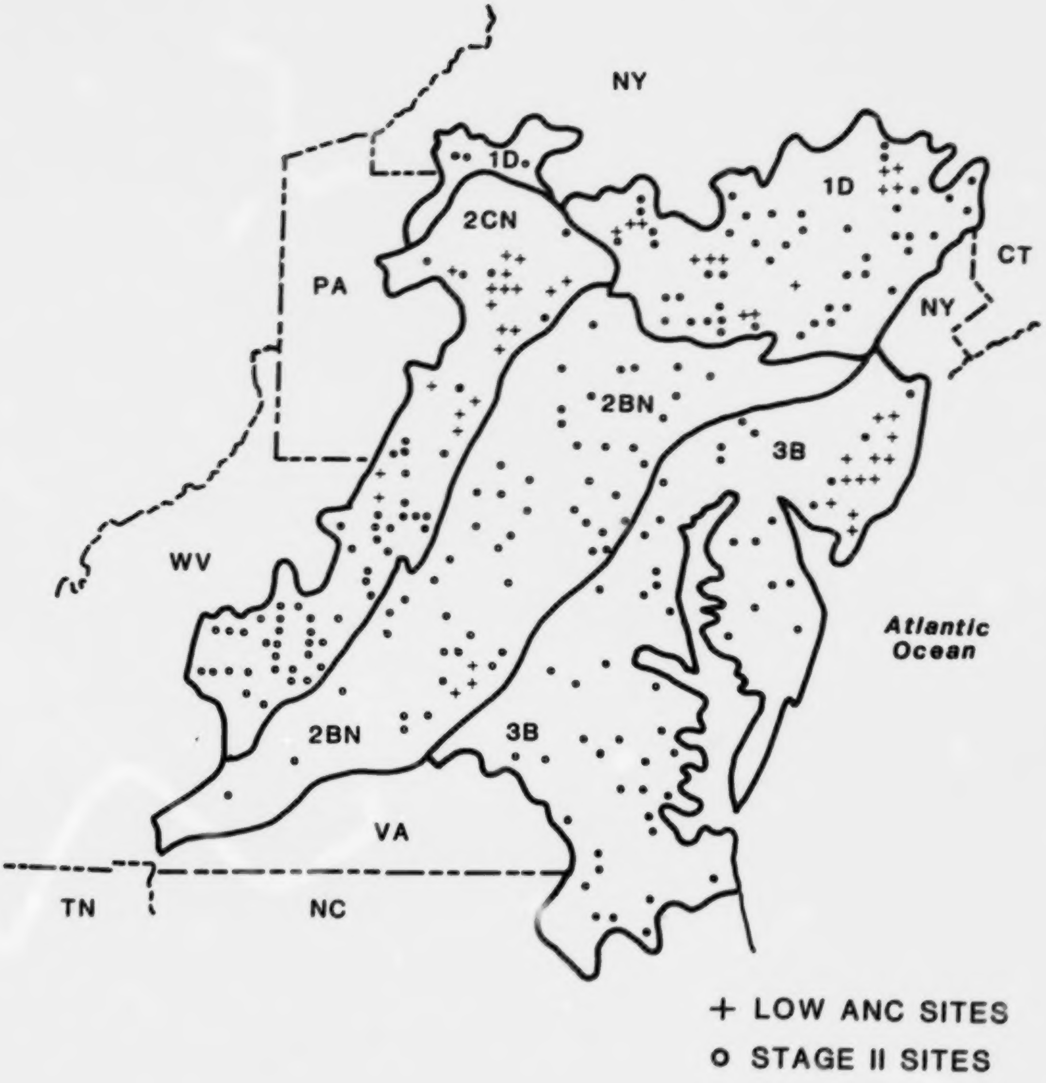

NY
1D
1D
2CN
CT
PA
NY
2BN
3B
WV
Atlantic Ocean
2BN
3B
VA
TN
NC
+ LOW ANC SITES
o STAGE II SITES

Figure 5.4. National Stream Survey Mid-Atlantic Phase I Survey second stage sampling sites. Note: Low ANC sites have ANC less than 50 μeq/L.

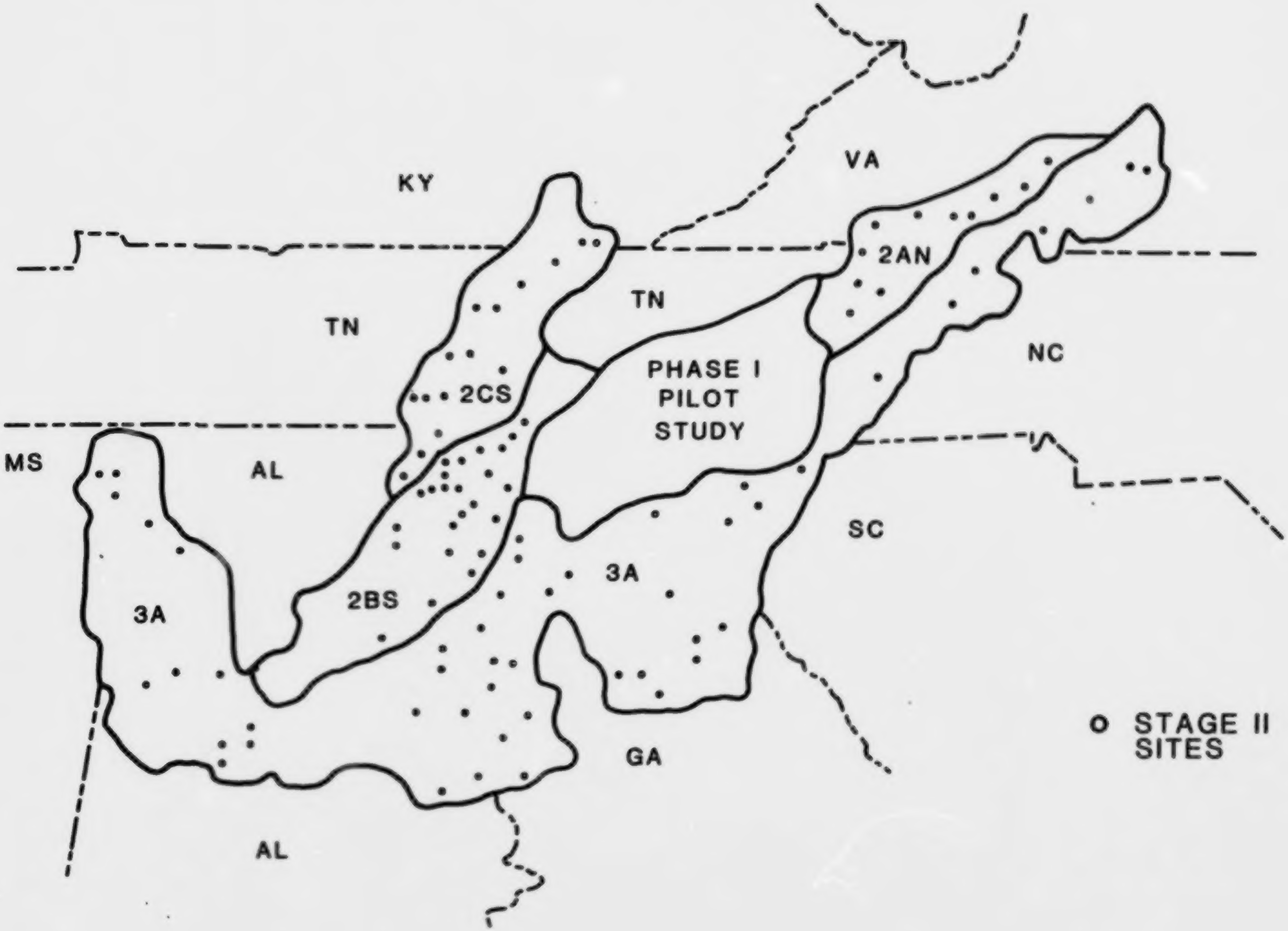

KY
VA
TN
TN
2CS
2AN
NC
PHASE I
PILOT
STUDY
MS
AL
SC
3A
3A
2BS
GA
AL
o STAGE II
SITES

Figure 5.5. National Stream Survey Southeast Screening Survey second stage sampling sites, Southern Appalachian subregions.

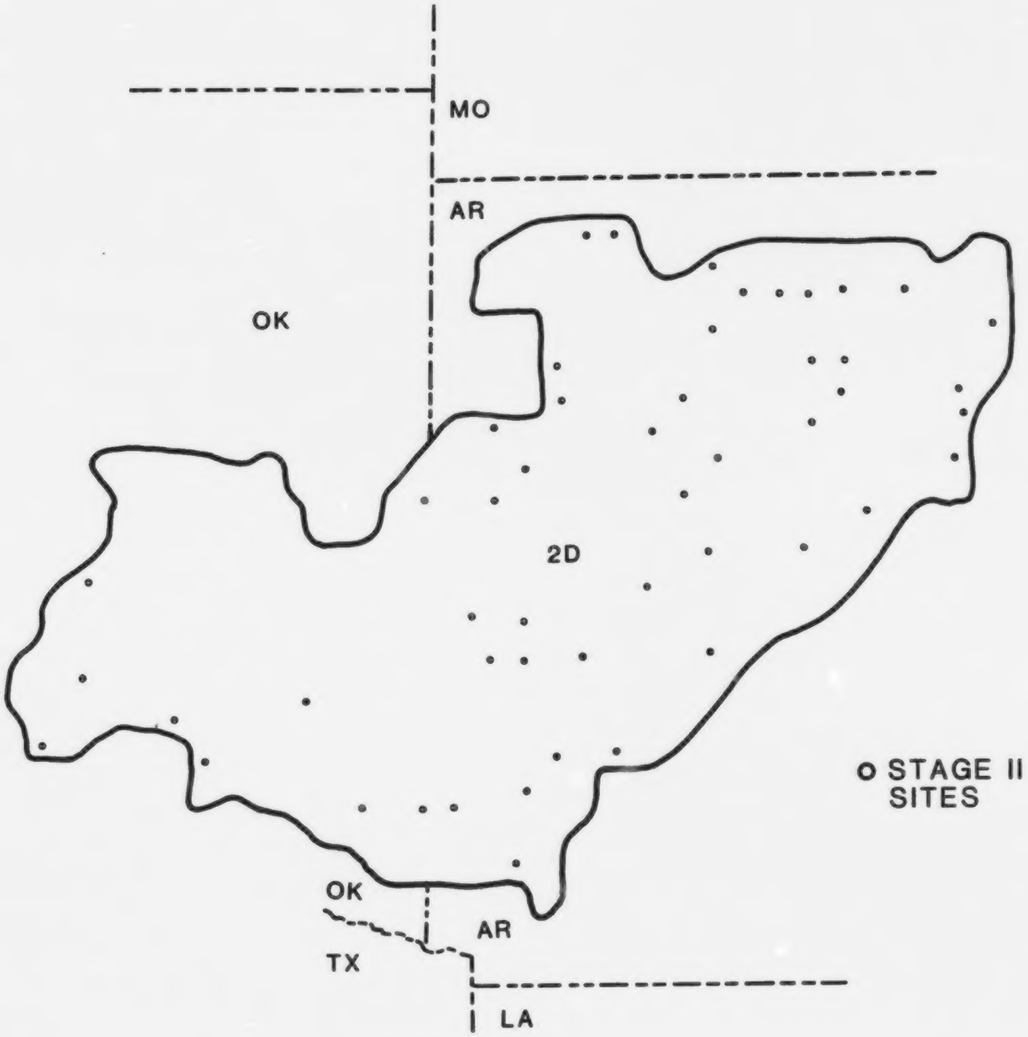

MO
AR
OK
2D
OK
AR
TX
LA
o STAGE II SITES

Figure 5.6. National Stream Survey Southeast Screening Survey second stage sampling sites, Ozark and Ouachita Mountains subregion.

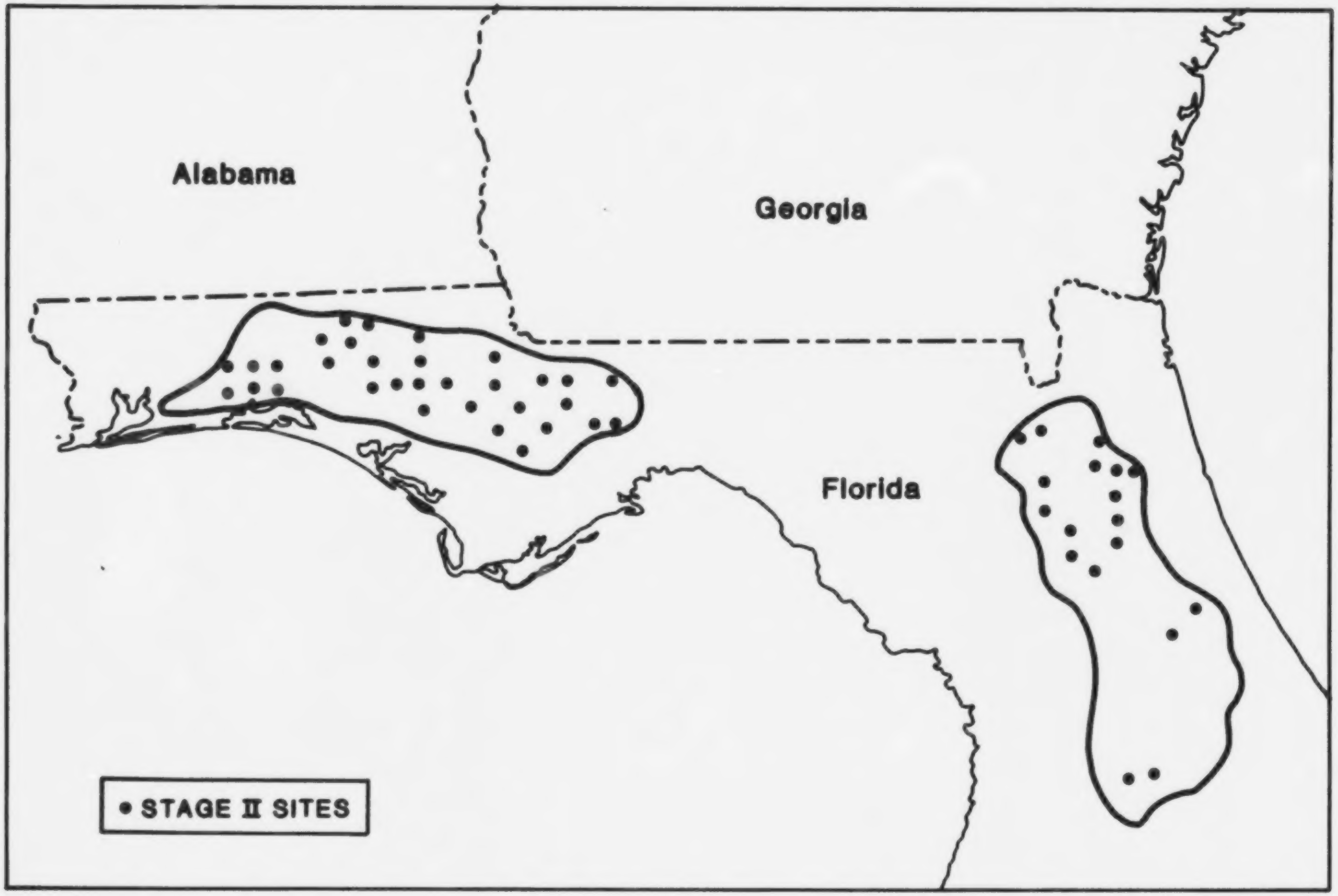

Alabama
Georgia
Florida
● STAGE II SITES

Figure 5.7. National Stream Survey Southeast Screening Survey second stage sampling sites, Florida subregion.

TABLE 5.1. PARAMETERS TO BE MEASURED DURING PHASE I OF THE NATIONAL STREAM SURVEY

Site Measurement	In Situ Measurement	Laboratory Measurement
gauge height (stage-Phase I surveys only)	temperature	pH (closed)[a]
	specific conductance	pH (air equilibrated)
stream width	dissolved oxygen	pH (open system)
stream depth		DIC[b]
land use		DIC, air equilibrated
bank vegetation		DOC
stream substrate		true color[a]
stream substrate	Streamside Measurement	turbidity[a]
cloud cover		specific conductance[b]
weather conditions	pH (open system)	ANC
watershed disturbances		BNC
elevation		aluminum (total)
		aluminum (total extractable)
		aluminum (nonexchangeable and total PCV reactive)[a]
		aluminum (organic extractable)
		calcium
		magnesium
		potassium
		sodium
		nitrate
		sulfate
		chloride
		fluoride
		silica
		iron
		ammonium
		manganese
		phosphorus (total dissolved[c])

[a] Determined at the mobile processing laboratory only.

[b] Determined at the mobile processing laboratory and at the contract analytical laboratory.

[c] For the Phase I - Pilot Survey, total phosphorus was determined (samples were unfiltered). For the Mid-Atlantic Phase I, Southeast Screening and Episodes Pilot Surveys, total dissolved phosphorus was determined (samples were filtered).

maps, and inputs from springs and seeps that feed the reach. For population description, it is the way that a particular chemical value characterizes the reach length (or some transformation such as habitat area) that is of interest. Therefore, variation in chemical values along the reach must be measured or inferred. For the Mid-Atlantic Phase I Survey, samples are collected during the spring sampling season on each of two sampling dates at the upstream and downstream nodes of each reach. For the Phase I surveys, streams are not sampled during major hydrologic events (defined as flows in excess of twice spring baseflow). Sampling during these events is conducted as part of the Episodes Pilot Survey.

Because the Southeast Screening Survey is targeted primarily at producing population estimates, only one sample is collected. Upstream and downstream nodes are sampled on each reach to provide population estimates based on lengths of reaches in each criterion range. In addition, sampling the upstream node provides information about watersheds too small to be included as direct drainages in the NSS target population. These very small headwaters watersheds may represent important "early warning" indicators in regions that are not receiving high inputs of atmospheric acids.

6.0 FIELD OPERATIONS

Field operations are conducted at four mobile field bases. Two of these field bases are located in Phase I areas. Each of these is staffed by a base coordinator, a logistics coordinator, and 5 two-person sampling teams. The other two field bases are located in Southeast Screening areas and are each staffed by a base coordinator, a logistics coordinator, and 2 two-person sampling teams. The base coordinator is responsible for the overall operation of the field base. The logistics coordinator assists the base coordinator. Each sampling team visits one or two streams a day. Each stream is sampled at its upstream and its downstream node. The sampling teams from each Phase I field base sample an average of seven streams per day, and the teams from each Southeast Screening base station sample an average of three streams per day. The overall total sample load under these average conditions is 44, including 2 duplicates and 2 blanks.

In the following sections, the activities of the field crews are summarized. A more detailed description of the field operations is given in the field manual (Hagley et al., 1986).

6.1 Sampling Team Activities

Each sampling crew consists of two scientists (except during episodics). It is their responsibility to perform all sampling operations correctly and to accurately record all data. The scientists must be qualified to operate all equipment and to follow prescribed procedures.

For each sampling trip, the activities of the sampling team are divided into (1) activities at the field base conducted prior to arrival at the stream site, (2) activities at the stream site, and (3) activities following sample collection. The following subsections describe the activities in detail. A flow scheme of sampling team activities is shown in Figure 6.1.

6.1.1 Field Base Activities Before Sampling Trip - Prior to leaving the field base the sampling team:

- Prepares a daily itinerary of sites to be sampled, routes of travel to and between sites, and personal identification information. This itinerary is given to the field base coordinator.
- Ensures that all necessary equipment and supplies are present.
- Calibrates pH, and dissolved oxygen (DO) meters used to obtain pH, temperature, and DO measurements of each stream; checks the calibration of the conductance and flow meters used to measure specific conductance and flow velocity. The QA/QC procedures are described in detail in Section 7 of this QA plan. QCCS, pH calibration

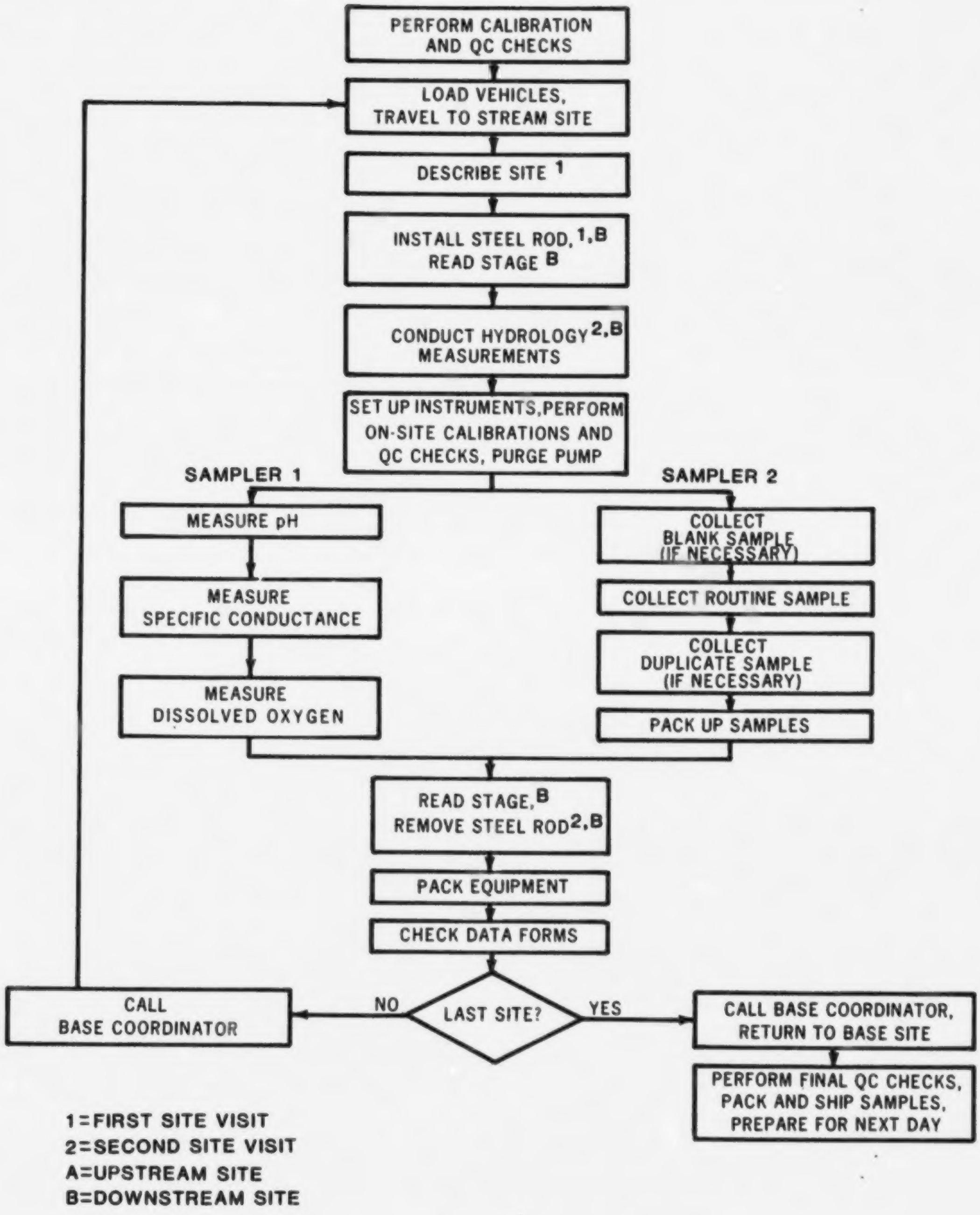

PERFORM CALIBRATION AND QC CHECKS
LOAD VEHICLES, TRAVEL TO STREAM SITE
DESCRIBE SITE 1
INSTALL STEEL ROD, 1,B READ STAGE B
CONDUCT HYDROLOGY 2,B MEASUREMENTS
SET UP INSTRUMENTS, PERFORM ON-SITE CALIBRATIONS AND QC CHECKS, PURGE PUMP
SAMPLER 1
SAMPLER 2
MEASURE pH
MEASURE SPECIFIC CONDUCTANCE
MEASURE DISSOLVED OXYGEN
COLLECT BLANK SAMPLE (IF NECESSARY)
COLLECT ROUTINE SAMPLE
COLLECT DUPLICATE SAMPLE (IF NECESSARY)
PACK UP SAMPLES
READ STAGE, B REMOVE STEEL ROD 2,B
PACK EQUIPMENT
CHECK DATA FORMS
LAST SITE?
NO
YES
CALL BASE COORDINATOR
CALL BASE COORDINATOR, RETURN TO BASE SITE
PERFORM FINAL QC CHECKS, PACK AND SHIP SAMPLES, PREPARE FOR NEXT DAY
1=FIRST SITE VISIT
2=SECOND SITE VISIT
A=UPSTREAM SITE
B=DOWNSTREAM SITE

Figure 6.1. Flowchart of sampling activities for the National Stream Survey.

buffers, and any other reagents needed at the site are prepared previously in a laboratory or are purchased. No reagent preparation is performed in the field.

- Reviews a detailed reconnaissance sheet that describes roads and trails and gives distances to the sampling site.

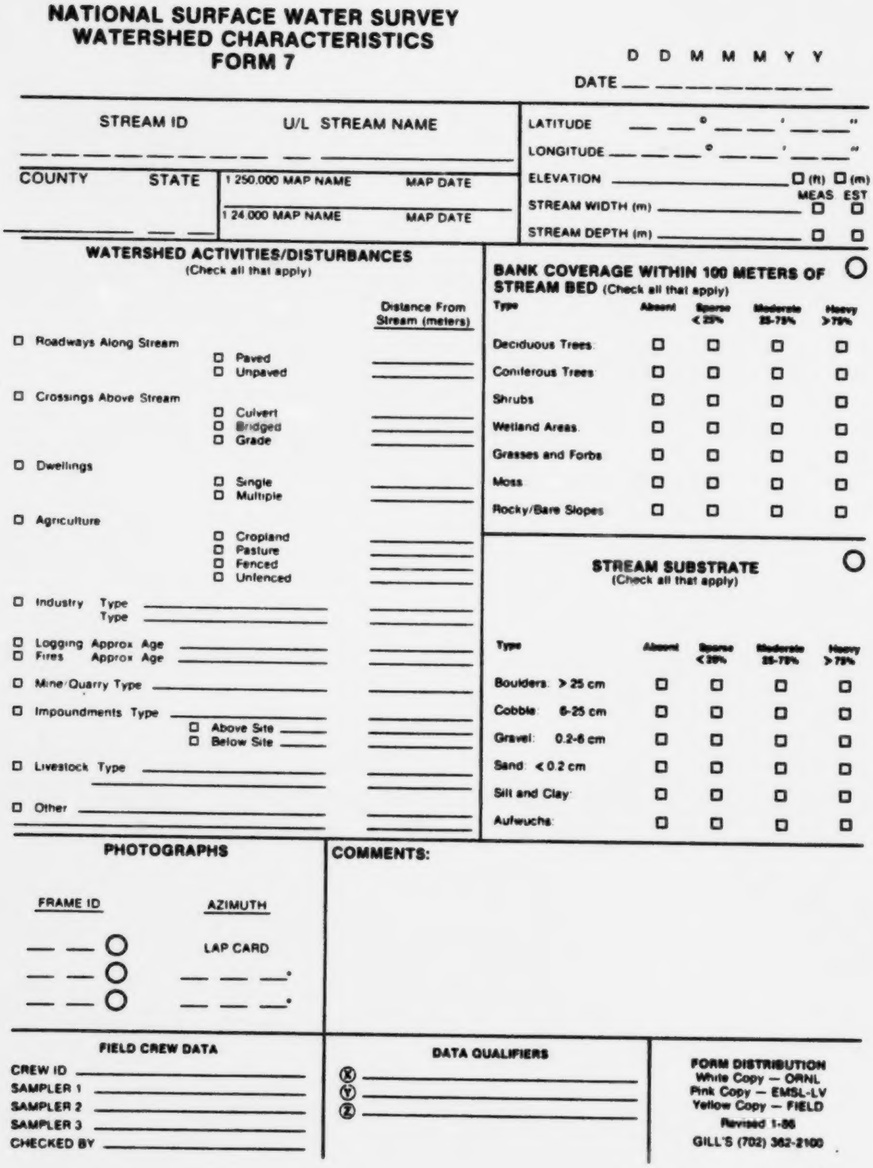
6.1.2 Stream Site Activities - On the first visit to each stream site, watershed characteristics, including elevation location, stream width and mean depth, disturbances, vegetative cover, and stream substrate are noted on Form 7 (Watershed Characteristics - Figure 6.2). Stream stage (for Phase I streams), percent cloud cover, recent or current rainfall, stream temperature, and visit number are noted on Form 4 (Stream Data Form, see Figure 6.3).

In addition, on the first visit, photographs are taken of the areas upstream and downstream from the sampling site. Before the set of stream photographs is taken, a lap card is photographed that shows the date and stream name, stream and team ID numbers, and frame number. After the photographs are taken, the photograph numbers are recorded on NSWS Form 7 (Watershed Characteristics). The exact sampling site is marked on a 1:24,000-scale topographic map, and the site coordinates are determined and are entered on Form 7.

For Southeast Screening streams, hydrologic discharge components (width, flow, and average channel depth) are estimated at each downstream site and are recorded on NSWS Form 4A (Hydrologic Data - Figure 6.4). For Phase I streams, discharge components are measured on the second visit to each downstream site and are recorded on Form 4A.

During Episodes Pilot sampling, precipitation, pH, temperature, conductance, and DO are measured periodically; water samples are collected and discharge measurements are taken at the appropriate times. Data are recorded on NSWS Form 6 (Stream Episode Data - Figure 6.5).

6.1.2.1 Sample collection - The team member collecting water samples sets up the peristaltic pump using new Tygon tubing. If required, a field blank sample is collected first. The pump tubing is rinsed with deionized (DI) water for 2 minutes, and a clean Cubitainer is rinsed three times with DI water from one of two Cubitainers of water carried to the sampling site for this purpose. A blank sample is collected in the rinsed Cubitainer from the second Cubitainer of water. Two syringe samples taken from the blank are used for the aluminum analyses. Field blank samples are taken before routine and duplicate samples. A new piece of tubing is attached to a sampling boom and is submerged in midstream. The tubing is rinsed with stream water for 2 minutes (pump flow rate about 2 L/min). A clean Cubitainer is rinsed three times with 100 to 200 mL stream water, then is filled. It is imperative



NATIONAL SURFACE WATER SURVEY
WATERSHED CHARACTERISTICS
FORM 7

DATE __ __ __ __ __ __ __ (D D M M M Y Y)

STREAM ID __ __ __ __ __ __ __ __
U/L __
STREAM NAME ____________________

LATITUDE __ __ ° __ __ ' __ __ "
LONGITUDE __ __ __ ° __ __ ' __ __ "
ELEVATION ____________ ☐ (ft) ☐ (m)

	MEAS	EST
STREAM WIDTH (m) ____________	☐	☐
STREAM DEPTH (m) ____________	☐	☐

COUNTY ____________
STATE __ __
1:250,000 MAP NAME ____________ MAP DATE ____________
1:24,000 MAP NAME ____________ MAP DATE ____________

WATERSHED ACTIVITIES/DISTURBANCES
(Check all that apply)

Distance From Stream (meters)

- ☐ Roadways Along Stream
  - ☐ Paved ________
  - ☐ Unpaved ________
- ☐ Crossings Above Stream
  - ☐ Culvert ________
  - ☐ Bridged ________
  - ☐ Grade ________
- ☐ Dwellings
  - ☐ Single ________
  - ☐ Multiple ________
- ☐ Agriculture
  - ☐ Cropland ________
  - ☐ Pasture ________
  - ☐ Fenced ________
  - ☐ Unfenced ________
- ☐ Industry Type ____________ ________
  - Type ____________ ________
- ☐ Logging Approx Age ____________ ________
- ☐ Fires Approx Age ____________ ________
- ☐ Mine/Quarry Type ____________ ________
- ☐ Impoundments Type ____________ ________
  - ☐ Above Site ________ ________
  - ☐ Below Site ________ ________
- ☐ Livestock Type ____________ ________
- ☐ Other ____________ ________

BANK COVERAGE WITHIN 100 METERS OF STREAM BED (Check all that apply) ○

Type	Absent	Sparse <25%	Moderate 25-75%	Heavy >75%
Deciduous Trees:	☐	☐	☐	☐
Coniferous Trees:	☐	☐	☐	☐
Shrubs:	☐	☐	☐	☐
Wetland Areas:	☐	☐	☐	☐
Grasses and Forbs:	☐	☐	☐	☐
Moss:	☐	☐	☐	☐
Rocky/Bare Slopes:	☐	☐	☐	☐

STREAM SUBSTRATE ○
(Check all that apply)

Type	Absent	Sparse <25%	Moderate 25-75%	Heavy >75%
Boulders: > 25 cm	☐	☐	☐	☐
Cobble: 6-25 cm	☐	☐	☐	☐
Gravel: 0.2-6 cm	☐	☐	☐	☐
Sand: < 0.2 cm	☐	☐	☐	☐
Silt and Clay:	☐	☐	☐	☐
Aufwuchs:	☐	☐	☐	☐

PHOTOGRAPHS

FRAME ID	AZIMUTH
__ __ ○	LAP CARD
__ __ ○	__ __ __°
__ __ ○	__ __ __°

COMMENTS:

FIELD CREW DATA
CREW ID ____________
SAMPLER 1 ____________
SAMPLER 2 ____________
SAMPLER 3 ____________
CHECKED BY ____________

DATA QUALIFIERS
Ⓧ ____________
Ⓨ ____________
Ⓩ ____________

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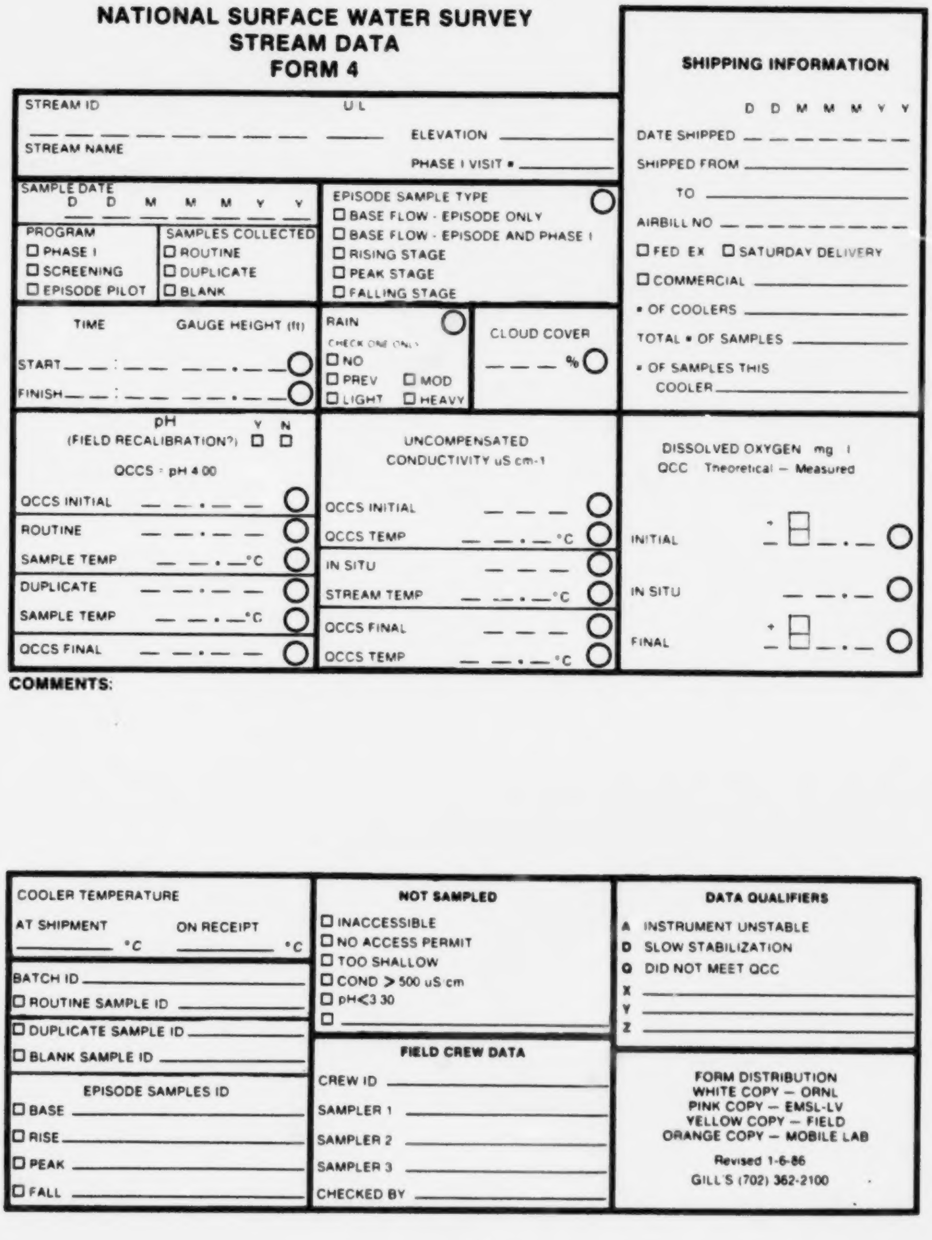
Figure 6.2. National Surface Water Survey Form 7 - Watershed Characteristics.



NATIONAL SURFACE WATER SURVEY
STREAM DATA
FORM 4

STREAM ID
U L
ELEVATION
STREAM NAME
PHASE I VISIT #

SAMPLE DATE
D D M M M Y Y

PROGRAM
☐ PHASE I
☐ SCREENING
☐ EPISODE PILOT

SAMPLES COLLECTED
☐ ROUTINE
☐ DUPLICATE
☐ BLANK

EPISODE SAMPLE TYPE ○
☐ BASE FLOW - EPISODE ONLY
☐ BASE FLOW - EPISODE AND PHASE I
☐ RISING STAGE
☐ PEAK STAGE
☐ FALLING STAGE

TIME
GAUGE HEIGHT (ft)
START ○
FINISH ○

RAIN ○
CHECK ONE ONLY
☐ NO
☐ PREV ☐ MOD
☐ LIGHT ☐ HEAVY

CLOUD COVER
% ○

pH
(FIELD RECALIBRATION?) Y ☐ N ☐
QCCS = pH 4.00
QCCS INITIAL ○
ROUTINE ○
SAMPLE TEMP °C ○
DUPLICATE ○
SAMPLE TEMP °C ○
QCCS FINAL ○

UNCOMPENSATED
CONDUCTIVITY uS cm-1
QCCS INITIAL ○
QCCS TEMP °C ○
IN SITU ○
STREAM TEMP °C ○
QCCS FINAL ○
QCCS TEMP °C ○

SHIPPING INFORMATION
D D M M M Y Y
DATE SHIPPED
SHIPPED FROM
TO
AIRBILL NO
☐ FED EX ☐ SATURDAY DELIVERY
☐ COMMERCIAL
OF COOLERS
TOTAL # OF SAMPLES
OF SAMPLES THIS COOLER

DISSOLVED OXYGEN mg l
QCC Theoretical – Measured
INITIAL ± ○
IN SITU ○
FINAL ± ○

COMMENTS:

COOLER TEMPERATURE
AT SHIPMENT °C
ON RECEIPT °C

BATCH ID
☐ ROUTINE SAMPLE ID
☐ DUPLICATE SAMPLE ID
☐ BLANK SAMPLE ID

EPISODE SAMPLES ID
☐ BASE
☐ RISE
☐ PEAK
☐ FALL

NOT SAMPLED
☐ INACCESSIBLE
☐ NO ACCESS PERMIT
☐ TOO SHALLOW
☐ COND > 500 uS cm
☐ pH<3.30
☐

FIELD CREW DATA
CREW ID
SAMPLER 1
SAMPLER 2
SAMPLER 3
CHECKED BY

DATA QUALIFIERS
A INSTRUMENT UNSTABLE
D SLOW STABILIZATION
Q DID NOT MEET QCC
X
Y
Z

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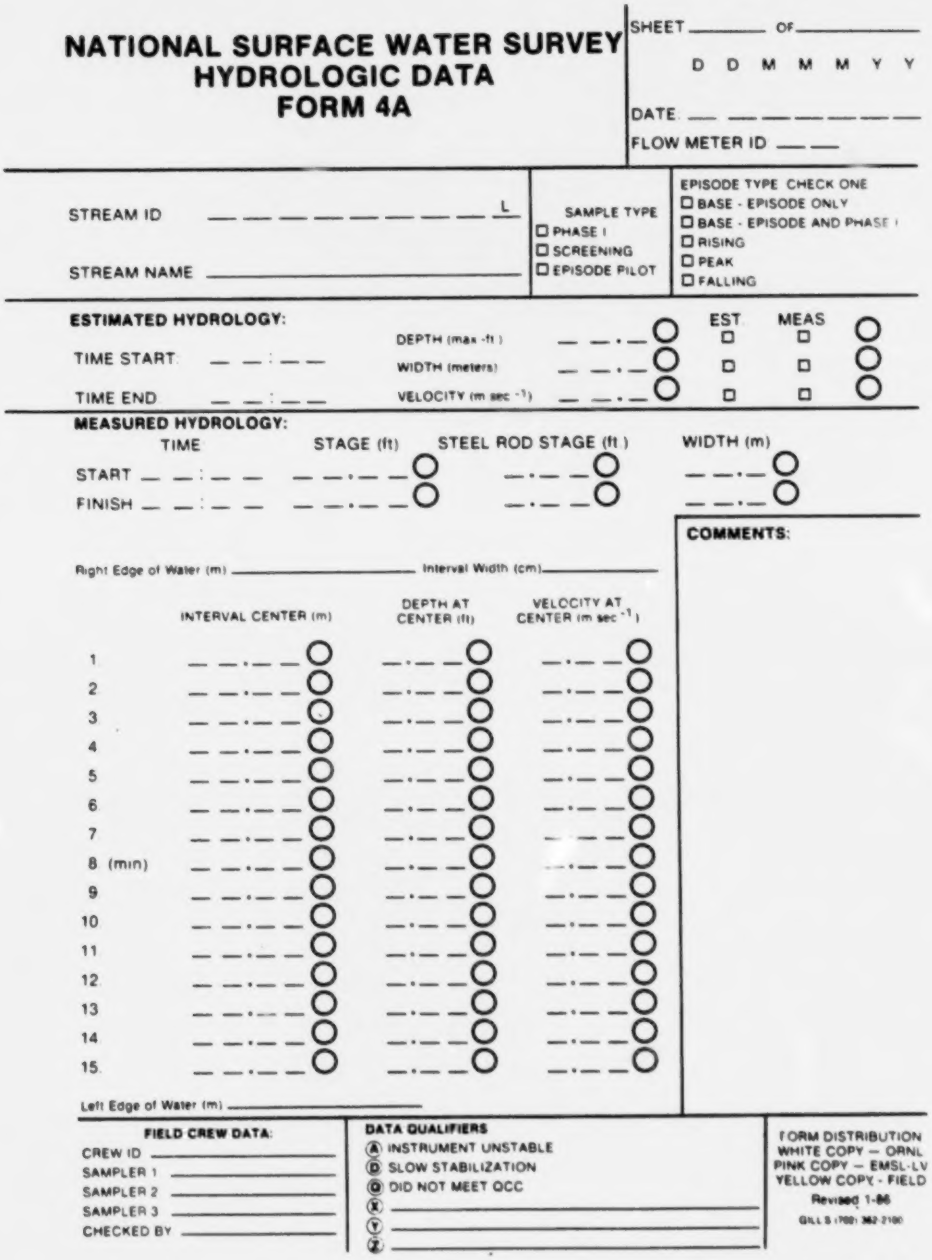
Figure 6.3. National Surface Water Survey Form 4 - Stream Data.



NATIONAL SURFACE WATER SURVEY
HYDROLOGIC DATA
FORM 4A

SHEET ______ OF ______

DATE D D M M M Y Y

FLOW METER ID __ __

STREAM ID __ __ __ __ __ __ __ __ L

STREAM NAME ______________________

SAMPLE TYPE
☐ PHASE I
☐ SCREENING
☐ EPISODE PILOT

EPISODE TYPE CHECK ONE
☐ BASE - EPISODE ONLY
☐ BASE - EPISODE AND PHASE I
☐ RISING
☐ PEAK
☐ FALLING

ESTIMATED HYDROLOGY:

TIME START __ __ : __ __

TIME END __ __ : __ __

			EST.	MEAS	
DEPTH (max - ft)	__ __ . __	○	☐	☐	○
WIDTH (meters)	__ __ . __	○	☐	☐	○
VELOCITY (m sec $^{-1}$)	__ __ . __	○	☐	☐	○

MEASURED HYDROLOGY:

	TIME	STAGE (ft)	STEEL ROD STAGE (ft.)	WIDTH (m)
START	__ __ : __ __	__ __ . __ __ ○	__ . __ __ ○	__ __ . __ ○
FINISH	__ __ : __ __	__ __ . __ __ ○	__ . __ __ ○	__ __ . __ ○

COMMENTS:

Right Edge of Water (m) ______________ Interval Width (cm) ______________

	INTERVAL CENTER (m)	DEPTH AT CENTER (ft)	VELOCITY AT CENTER (m sec $^{-1}$)
1	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
2	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
3	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
4	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
5	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
6	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
7	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
8 (min)	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
9	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
10	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
11	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
12	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
13	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
14	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○
15	__ __ . __ __ ○	__ . __ __ ○	__ . __ __ ○

Left Edge of Water (m) ______________

FIELD CREW DATA:
CREW ID ______________
SAMPLER 1 ______________
SAMPLER 2 ______________
SAMPLER 3 ______________
CHECKED BY ______________

DATA QUALIFIERS
Ⓐ INSTRUMENT UNSTABLE
Ⓓ SLOW STABILIZATION
Ⓠ DID NOT MEET QCC
Ⓧ ______________
Ⓨ ______________
Ⓩ ______________

FORM DISTRIBUTION
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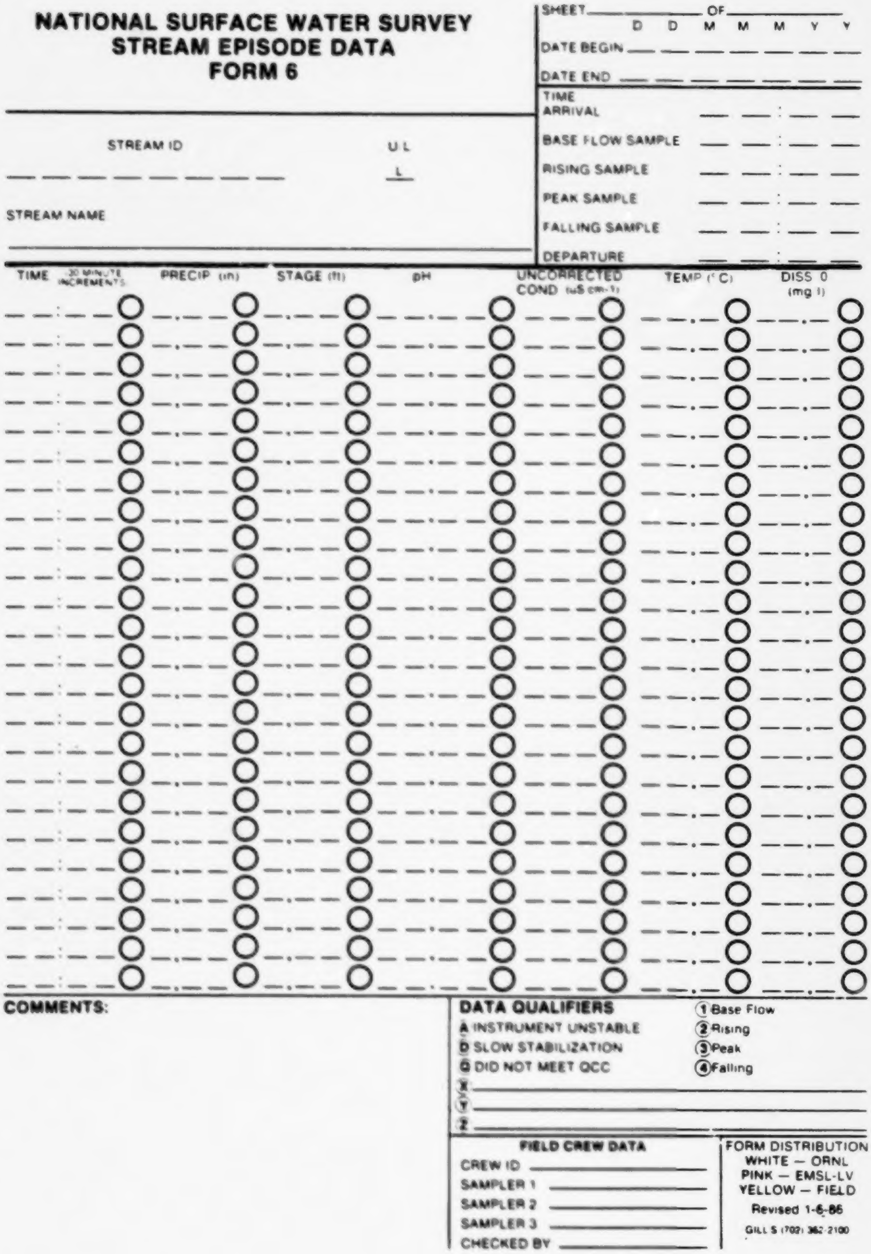
Figure 6.4. National Surface Water Survey Form 4A - Hydrologic Data.



**NATIONAL SURFACE WATER SURVEY
STREAM EPISODE DATA
FORM 6**

SHEET ______ OF ______

	D	D	M	M	M	Y	Y
DATE BEGIN	__	__	__	__	__	__	__
DATE END	__	__	__	__	__	__	__

TIME
ARRIVAL __ __ : __ __
BASE FLOW SAMPLE __ __ : __ __
RISING SAMPLE __ __ : __ __
PEAK SAMPLE __ __ : __ __
FALLING SAMPLE __ __ : __ __
DEPARTURE __ __ : __ __

STREAM ID __ __ __ __ __ __ __ __

U L
L

STREAM NAME ____________________

TIME 30 MINUTE INCREMENTS	PRECIP (in)	STAGE (ft)	pH	UNCORRECTED COND (uS cm-1)	TEMP (°C)	DISS O (mg l)
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○
__ __ : __ __ ○	__ . __ __ ○	__ . __ __ ○	__ __ . __ __ ○	__ __ __ ○	__ __ . __ ○	__ __ . __ ○

COMMENTS:

DATA QUALIFIERS
A INSTRUMENT UNSTABLE
D SLOW STABILIZATION
Q DID NOT MEET QCC
X ____________________
Y ____________________
Z ____________________

① Base Flow
② Rising
③ Peak
④ Falling

FIELD CREW DATA
CREW ID ______________
SAMPLER 1 ______________
SAMPLER 2 ______________
SAMPLER 3 ______________
CHECKED BY ______________

FORM DISTRIBUTION
WHITE — ORNL
PINK — EMSL-LV
YELLOW — FIELD
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Figure 6.5. National Surface Water Survey Form 6 - Stream Episode Data.

that the tubing orifice does not come into contact with the ground or other sources of contamination. Next, four syringe samples are collected and are sealed with syringe valves. The syringes used are not acid-rinsed.

Before sample collection, the sample containers are labeled, and appropriate sample types are checked on the field sample label (Figure 6.6). After collection, samples are placed in coolers at 4°C for shipment to the mobile processing laboratory.

When required, duplicate samples are collected from each sampling region. The procedure used to collect duplicate samples is the same procedure used to collect routine samples.

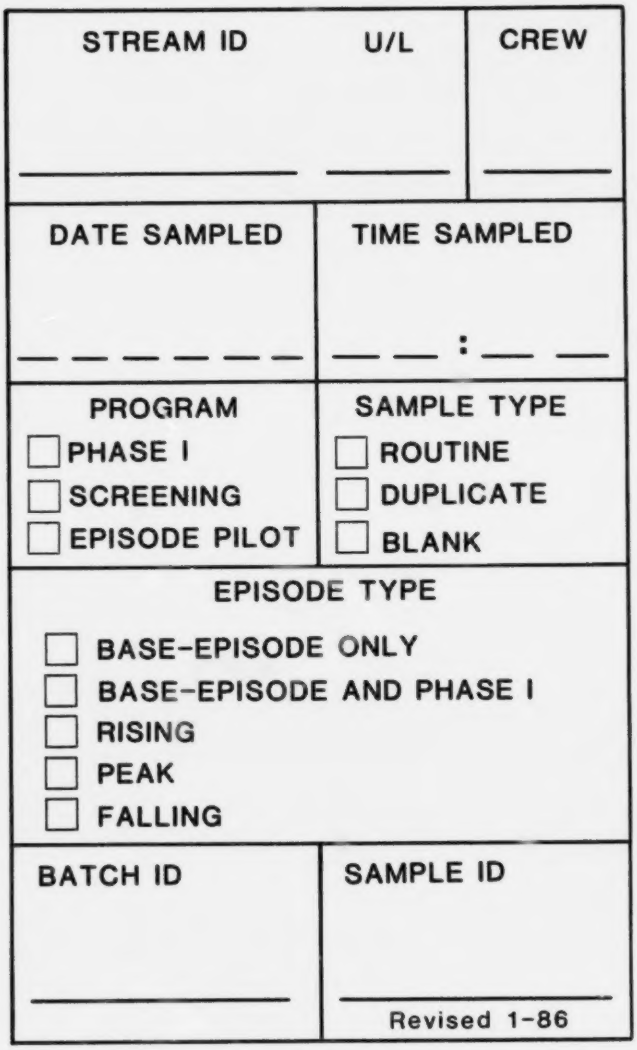
While one sampler collects the samples and aliquots and makes the stage and hydrologic measurements (if necessary), the other sampler sets up instruments and begins calibration procedures. The dissolved oxygen (DO) probe is placed in a watertight, moist container and is lowered into the stream to allow temperature equilibration. The calibration of the pH meter is checked by measuring a QCCS solution. If the pH meter does not meet QC limits, it is recalibrated in the field using pH 4 and pH 7 buffers. An open pH measurement is made as described in the field manual (Hagley et al., 1986). The conductance meter is checked using a QCCS, and in situ conductance and temperature measurements are made. Next, the calibration procedure for the DO meter is completed, and an in situ DO measurement is made.

If duplicate samples are collected, a duplicate set of pH measurements is taken. The sampler who performs pH measurements records all data in the field logbook. Duplicate DO and conductance readings are not made.

After all measurements have been made, the meters and probes are turned off and are returned to their carrying cases for transport to the vehicles. Final measurements of stream-gauge height and time are recorded, and the team returns to the vehicle with all gear, samples, and trash.

On arrival at the vehicle, the equipment is loaded for transport, and all data in the field logbook are transferred to the Stream Data Form, Form 4.

The sampling team proceeds to the next stream site where the same activities are performed.



STREAM ID	**U/L**	**CREW**
__________	______	______

DATE SAMPLED	**TIME SAMPLED**
_ _ _ _ _ _	_ _ : _ _
PROGRAM	**SAMPLE TYPE**
☐ PHASE I	☐ ROUTINE
☐ SCREENING	☐ DUPLICATE
☐ EPISODE PILOT	☐ BLANK

EPISODE TYPE

☐ BASE-EPISODE ONLY
☐ BASE-EPISODE AND PHASE I
☐ RISING
☐ PEAK
☐ FALLING

BATCH ID	**SAMPLE ID**
__________	__________
	Revised 1-86

Figure 6.6. Field sample label.

6.1.3 Field Base Activities After Sampling Trip - After returning from the field, the sampling team:

- Checks the calibration of the DO meter and enters the "final" theoretical measured DO QC value on Form 4.
- Checks all data forms to ensure accuracy and completeness and gives them to the base coordinator, along with the samples.
- Checks the calibration of the pH and conductance meters if they did not meet calibration checks during the day.
- Records all post-sampling calibration check information on the calibration form.
- Performs maintenance on or troubleshoots problems with meters, if necessary, according to manufacturer's instructions.
- Stores the conductance and DO probes in DI water and the pH electrode in 3 M KCl.

6.2 Field Base and Mobile Processing Laboratory Activities

The field base and mobile processing laboratory activities are outlined in Figure 6.7.

The collected, labeled samples are shipped as soon as possible from the field base to the mobile processing laboratory by Federal Express. The supervisor and analysts at the mobile processing laboratory are responsible for preliminary measurements and sample processing. These activities are described below.

6.2.1 Reagent Preparation - Reagents for total extractable aluminum extractions and MIBK extractions, and for specific conductance, DIC, and pH determinations must be prepared before the samples arrive. Detailed reagent preparation procedures can be found in the methods manual (Hillman et al., 1986) and in the mobile processing laboratory operations manual (Chaloud et al., in preparation).

6.2.2 Sample Processing - The following steps describe sample processing operations. They are performed in the order given.

6.2.2.1 Sample Description and Identification - Samples are organized into batches that are processed together. A batch consists of all samples collected and processed on the same day, from the same survey, that are sent to one analytical laboratory. It is expected that there will be approximately 44 samples or fewer in a batch, including routine, duplicate, blank, and audit samples. Each batch is assigned a unique batch ID number, which is recorded on the labels of all samples (and

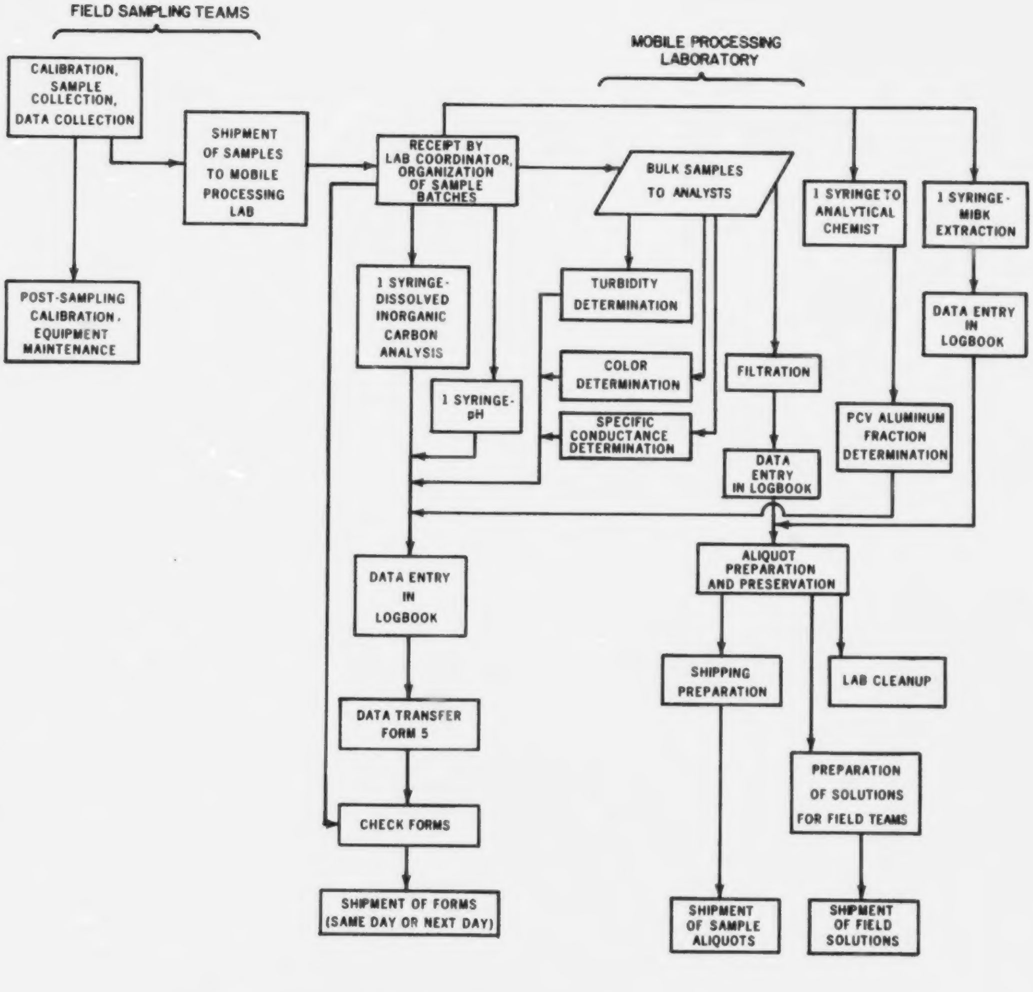

FIELD SAMPLING TEAMS
CALIBRATION, SAMPLE COLLECTION, DATA COLLECTION
POST-SAMPLING CALIBRATION, EQUIPMENT MAINTENANCE
SHIPMENT OF SAMPLES TO MOBILE PROCESSING LAB
MOBILE PROCESSING LABORATORY
RECEIPT BY LAB COORDINATOR, ORGANIZATION OF SAMPLE BATCHES
BULK SAMPLES TO ANALYSTS
1 SYRINGE TO ANALYTICAL CHEMIST
1 SYRINGE-MIBK EXTRACTION
1 SYRINGE-DISSOLVED INORGANIC CARBON ANALYSIS
TURBIDITY DETERMINATION
COLOR DETERMINATION
1 SYRINGE-pH
SPECIFIC CONDUCTANCE DETERMINATION
FILTRATION
DATA ENTRY IN LOGBOOK
PCV ALUMINUM FRACTION DETERMINATION
DATA ENTRY IN LOGBOOK
DATA ENTRY IN LOGBOOK
ALIQUOT PREPARATION AND PRESERVATION
SHIPPING PREPARATION
LAB CLEANUP
PREPARATION OF SOLUTIONS FOR FIELD TEAMS
DATA TRANSFER FORM 5
CHECK FORMS
SHIPMENT OF FORMS (SAME DAY OR NEXT DAY)
SHIPMENT OF SAMPLE ALIQUOTS
SHIPMENT OF FIELD SOLUTIONS

Figure 6.7. Flowchart of daily sampling and mobile processing laboratory activities for the National Stream Survey.

corresponding aliquots) in the batch. Each sample is then randomly assigned a sample ID number as follows:

Routine Samples - Five sample containers are filled at each stream: a syringe for DIC determination, a syringe for laboratory pH determination, a syringe for aluminum extraction (with MIBK), a syringe for PCV aluminum determinations, and a Cubitainer. One sample ID number is assigned to the five containers and is recorded on each container label.

Duplicate and Blank Samples - Sample ID numbers are assigned in the same manner as for the routine samples.

Field Audit Samples - Aliquots are prepared from one 2-L field audit sample (received each day from a central source) as shown on Table 6.1 and are included in each day's batch of samples. The label for the field and laboratory audit containers is shown in Figure 6.8. The code (Table 6.2) indicates the sample type and the concentrate lot number. A field audit sample is assigned a sample ID number in the same manner as a routine sample. The ID number is recorded on the label.

Laboratory Audit Samples - One or more lab audit sample(s) (received each day from a central source already prepared as aliquots) is included in each day's batch. A single lab audit sample consists of a set of seven aliquots (eight for the Phase I - Pilot Survey). Each aliquot has a temporary label like that in Figure 6.8b. An aliquot label (Figure 6.8c) is attached to each aliquot. The lab audit sample is then assigned a sample ID and batch number in the same manner as for a routine sample. The batch and sample ID numbers are recorded on each aliquot label. The date and the amount of preservative are also recorded on the label.

After the batch and sample ID numbers are assigned and are recorded on each sample label, the same information is entered on Form 5, Batch/QC Field Data (Figure 6.9). Also, the stream ID, the appropriate code for each sample (from Table 6.2), and the appropriate site or type ID (from Table 6.2) are entered on Form 5.

Note 1: The sample ID numbers are randomly assigned to all samples in a batch. Furthermore, sample ID numbers run consecutively from 1 to the number of samples in the batch. Audit samples must not always be assigned the same sample ID number.

Note 2: Field audit samples are processed exactly like routine stream samples. After the batch and sample ID numbers are assigned, the temporary audit label is removed from the audit sample and is placed in the audit logbook.

TABLE 6.1. ALIQUOTS, CONTAINERS, PRESERVATIVES, AND CORRESPONDING PARAMETERS

	Aliquot/(Container)							
	1 (250-mL)	2 (10-mL)	3 (250-mL)	4 (125-mL)	5 (500-mL)	6 (125-mL)	7 (125-mL)	8[b] (125-mL)
Preservative and Description[a]	Filtered pH <2 with HNO_3	Filtered MIBK-HQ Extract	Filtered	Filtered pH <2 with H_2SO_4	Unfiltered	Filtered[c] pH <2 with H_2SO_4	Unfiltered pH <2 with HNO_3	Filtered Ion-Exchanged MIBK-HQ Extract
Parameters	Ca	Total Extractable Al	Cl^-	DOC	pH	Total Dissolved P[c]	Total Al	Organic Extractable Al
	K		SO_4^{2-}	NH_4^+	ANC			
	Mg		F^-		BNC			
	Na		NO_3^-		Specific Conductance			
	Mn		SiO_2		DIC			
	Fe							

[a] Aliquots 2, 3, 4, 5, 6, and 8 must be stored at 4°C in the dark.
[b] Prepared for Phase I - Pilot Survey only.
[c] For Phase I - Pilot Survey only; the aliquot was unfiltered and total P was measured.

FIELD AUDIT SAMPLE	
Radian ID No.	
Date Shipped	Date Received
Code	
Batch	ID

a. Field Audit Sample Label

LAB AUDIT SAMPLE	
Aliquot No.	
Date Shipped	Date Received
Code	
Preservative Amount	

b. Lab Audit Sample Label

Aliquot ____________

Batch ID ____________
Sample ID ____________
Date Sampled ____________

Preservative ____________
Amount ____________
Parameters ____________

Note: The aliquot number, preservative, and parameters are preprinted on the aliquot labels.

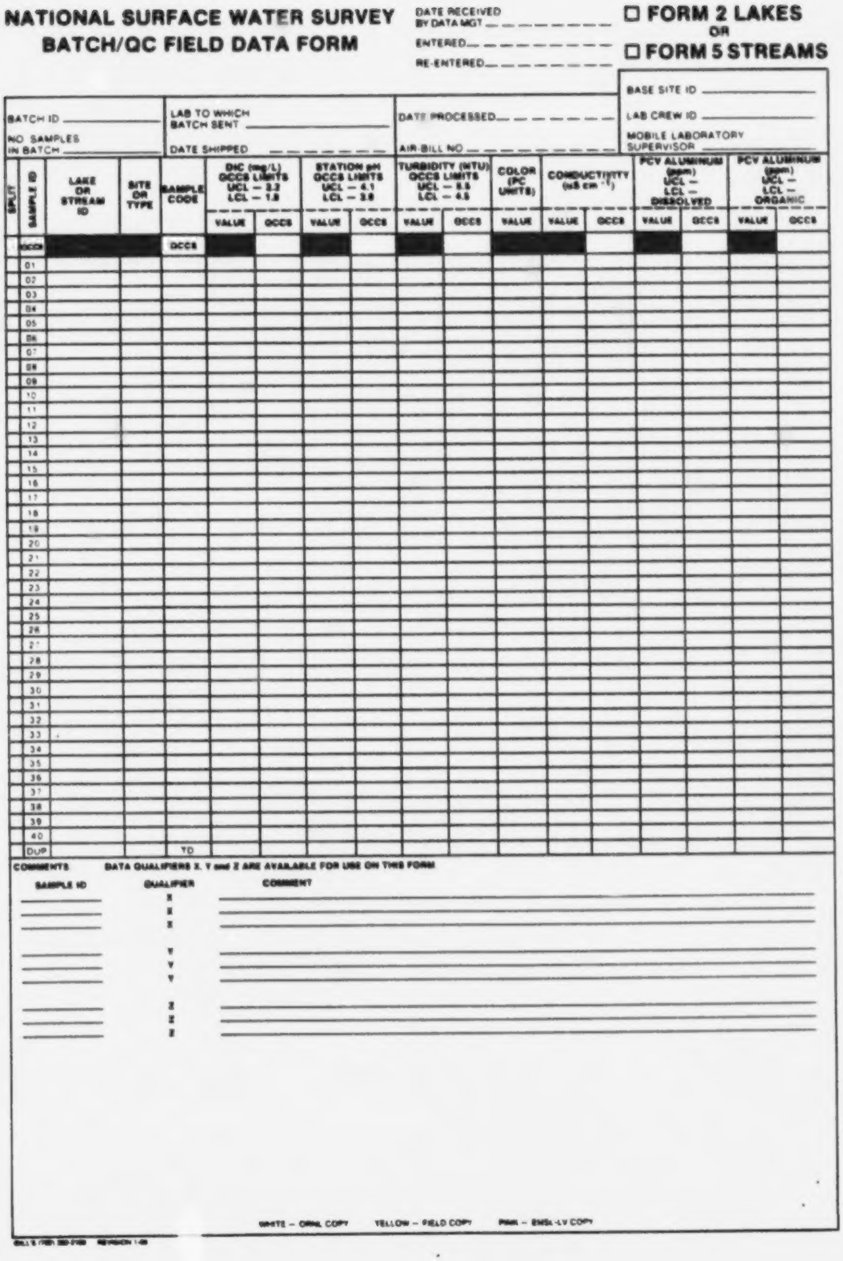
c. Aliquot Label

Figure 6.8. Aliquot and Audit Sample Labels.

TABLE 6.2. SAMPLE CODES

Sample Type	Code	Description
Normal[a,b]	R	Routine Stream Sample
	D	Duplicate Stream Sample
	B	Field Blank Sample
	TB	Mobile Processing Laboratory (Trailer) Blank
	TD	Mobile Processing Laboratory (Trailer) Duplicate
	QCCS	Quality Control Check Sample
Audit[b]	F L 1-001	
	001	Radian I.D. Number
	1	Concentrate lot number
	L	Concentration Level L = low, N = Natural
	F	Type of Audit Sample (F = Field, L = Lab)
Episodic[c]	EB	Episodic sample, base hydrograph
	ER	Episodic sample, rising hydrograph
	EP	Episodic sample, peak hydrograph
	EF	Episodic sample, falling hydrograph
	M1	Initial Mid-Atlantic Phase I Sample
	M2	Final Mid-Atlantic Phase I Sample
	S	Southeast Screening Sample

[a] Normal samples require a stream ID, except trailer blank.
[b] Recorded in sample code column on Batch/QC Field Data Form.
[c] Recorded in site or type column on Batch/QC Field Data Form.



NATIONAL SURFACE WATER SURVEY
BATCH/QC FIELD DATA FORM

DATE RECEIVED BY DATA MGT __________
ENTERED __________
RE-ENTERED __________

☐ **FORM 2 LAKES**
OR
☐ **FORM 5 STREAMS**

BASE SITE ID __________
LAB CREW ID __________
MOBILE LABORATORY SUPERVISOR __________

BATCH ID __________
NO SAMPLES IN BATCH __________
LAB TO WHICH BATCH SENT __________
DATE SHIPPED __________
DATE PROCESSED __________
AIR-BILL NO __________

SPLIT	SAMPLE ID	LAKE OR STREAM ID	SITE OR TYPE	SAMPLE CODE	DIC (mg/L) QCCS LIMITS UCL — 2.2 LCL — 1.8		STATION pH QCCS LIMITS UCL — 4.1 LCL — 3.9		TURBIDITY (NTU) QCCS LIMITS UCL — 5.5 LCL — 4.5		COLOR (PC UNITS)	CONDUCTIVITY ($\mu S\ cm^{-1}$)		PCV ALUMINUM (ppm) UCL — LCL — DISSOLVED		PCV ALUMINUM (ppm) UCL — LCL — ORGANIC	
					VALUE	QCCS	VALUE	QCCS	VALUE	QCCS	VALUE	VALUE	QCCS	VALUE	QCCS	VALUE	QCCS
	QCCS	■	■	QCCS	■		■		■		■	■		■		■	
	01																
	02																
	03																
	04																
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COMMENTS DATA QUALIFIERS X, Y and Z ARE AVAILABLE FOR USE ON THIS FORM

SAMPLE ID	QUALIFIER	COMMENT
	X	
	X	
	X	
	Y	
	Y	
	Y	
	Z	
	Z	
	Z	

WHITE – ORNL COPY YELLOW – FIELD COPY PINK – EMSL-LV COPY

Figure 6.9. National Surface Water Survey Form 5 - Batch/QC Field Data (National Stream Survey).

Note 3: Seven different aliquots (numbered as in Table 6.1) are prepared from each sample (routine, duplicate, audit, and blank samples). Each aliquot is assigned the same batch and sample ID numbers as the sample from which it is prepared. Aliquot 8 was prepared for the Phase I - Pilot Survey only.

Note 4: As soon as the 2-L field audit samples are received from the central source, four syringes of sample are taken (for the appropriate analyses) by the mobile processing laboratory coordinator. Two of the syringe samples are for aluminum determination using FIA and MIBK extraction, the third is for DIC, and the fourth is for pH determination. Any sample that remains after DIC determination may be used for pH determination, if necessary. All must be analyzed within 48 hours. Batch and sample ID numbers are assigned at the mobile processing laboratory and are recorded on the shipping form (Form 3, Figure 6.10).

Note 5: Copies of all field, laboratory, and streamside data forms are sent to the QA staff in Las Vegas, Nevada, daily.

6.2.2.2 DIC Determination - Immediately after assignment of batch and sample ID numbers, one analyst begins the DIC analyses. DIC is determined in routine, duplicate, and audit samples. The routine and duplicate samples are contained in sealed syringes (filled at the stream site). The results of the DIC determination are recorded on Form 5. The QC procedures are discussed in Section 7.

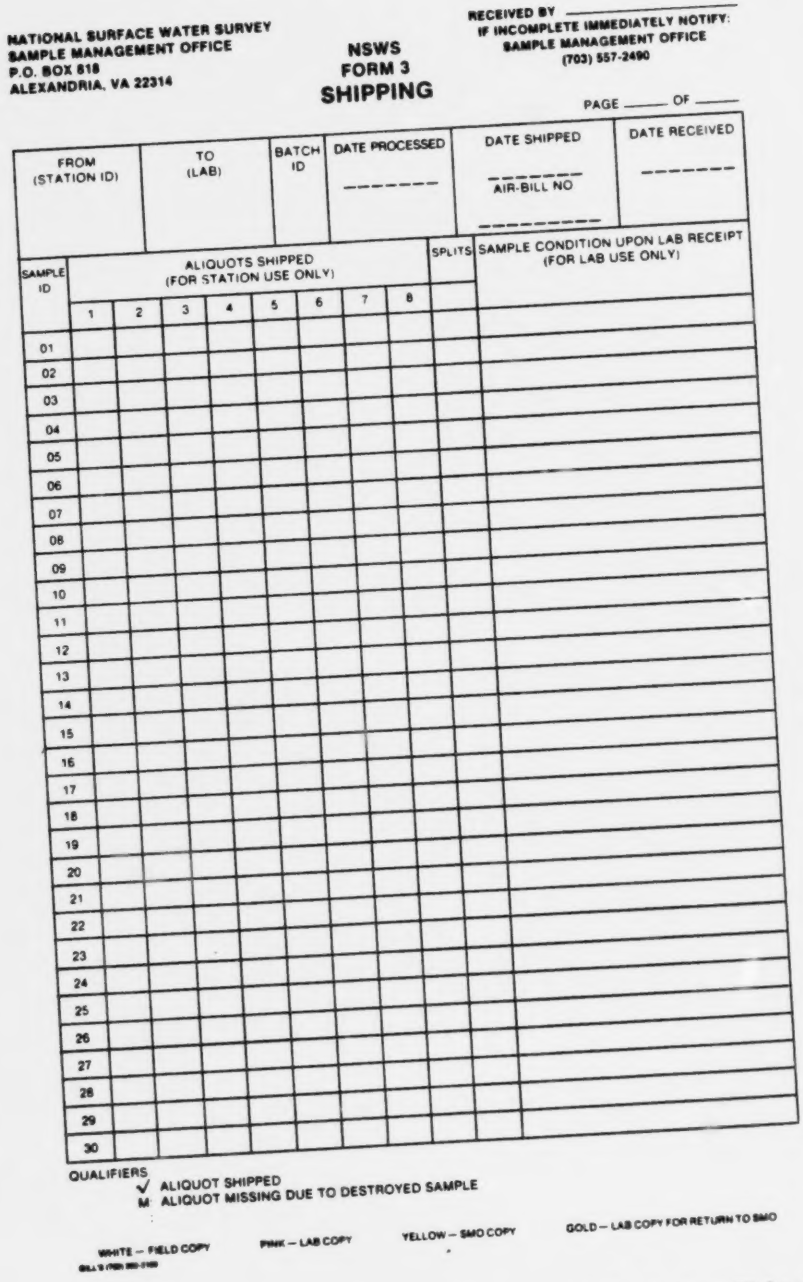
6.2.2.3 pH Determination (mobile processing laboratory) - After DIC determinations, the pH of the remaining sealed syringe sample is determined.

The QC procedures are discussed in Section 7. The results are recorded on Form 5. Copies of all raw data are sent to the QA staff in Las Vegas, Nevada, at survey completion or when requested.

Note: Two pH measurements are made: one at the stream site in an open beaker and one at the mobile processing laboratory in a sample chamber.

6.2.2.4 Sample Filtration, Preservation, and Aliquot Preparation - Eight aliquots from each Phase - I Pilot Survey sample and seven aliquots from each sample taken for other NSS surveys are prepared as specified in Table 6.1. Preparation of aliquots is described in the methods manual (Hillman et al., 1986).

6.2.2.5 True Color Determination - After centrifugation to remove turbidity, color is determined using Hach Model CO-1 Color Test Kit following the manufacturer's instructions. Results are recorded on Form 5. The QC procedures are discussed in Section 7.



NATIONAL SURFACE WATER SURVEY
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818
ALEXANDRIA, VA 22314

NSWS
FORM 3
SHIPPING

RECEIVED BY ______________
IF INCOMPLETE IMMEDIATELY NOTIFY:
SAMPLE MANAGEMENT OFFICE
(703) 557-2490

PAGE _____ OF _____

FROM (STATION ID)	TO (LAB)	BATCH ID	DATE PROCESSED	DATE SHIPPED	DATE RECEIVED
			--------	-------- AIR-BILL NO ----------	--------

SAMPLE ID	ALIQUOTS SHIPPED (FOR STATION USE ONLY)								SPLITS	SAMPLE CONDITION UPON LAB RECEIPT (FOR LAB USE ONLY)
	1	2	3	4	5	6	7	8		
01										
02										
03										
04										
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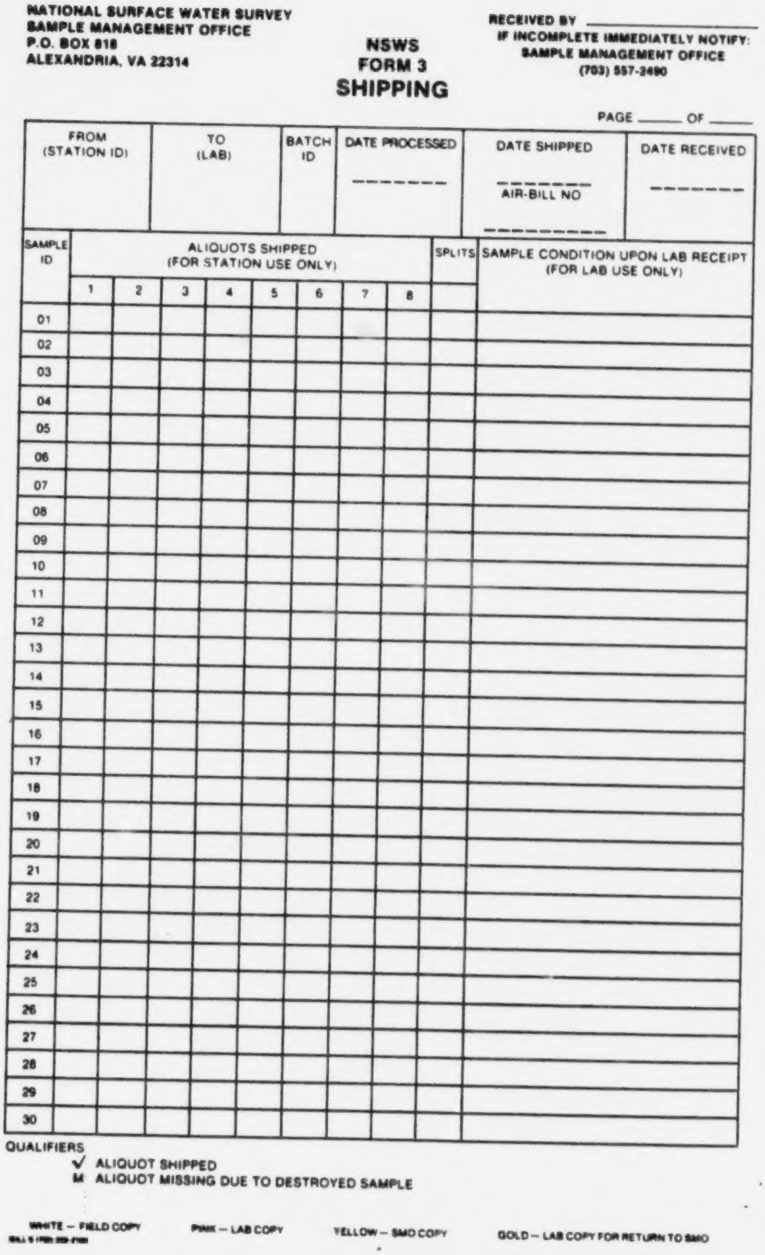
QUALIFIERS
✓ ALIQUOT SHIPPED
M ALIQUOT MISSING DUE TO DESTROYED SAMPLE

WHITE — FIELD COPY
PINK — LAB COPY
YELLOW — SMO COPY
GOLD — LAB COPY FOR RETURN TO SMO

Figure 6.10. National Surface Water Survey Form 3 - Shipping.



NATIONAL SURFACE WATER SURVEY
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818
ALEXANDRIA, VA 22314

NSWS
FORM 3
SHIPPING

RECEIVED BY ______________
IF INCOMPLETE IMMEDIATELY NOTIFY:
SAMPLE MANAGEMENT OFFICE
(703) 557-2490

PAGE _____ OF _____

FROM (STATION ID)	TO (LAB)	BATCH ID	DATE PROCESSED	DATE SHIPPED	DATE RECEIVED
			--------	-------- AIR-BILL NO ----------	--------

SAMPLE ID	ALIQUOTS SHIPPED (FOR STATION USE ONLY)								SPLITS	SAMPLE CONDITION UPON LAB RECEIPT (FOR LAB USE ONLY)
	1	2	3	4	5	6	7	8		
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QUALIFIERS
✓ ALIQUOT SHIPPED
M ALIQUOT MISSING DUE TO DESTROYED SAMPLE

WHITE — FIELD COPY   PINK — LAB COPY   YELLOW — SMO COPY   GOLD — LAB COPY FOR RETURN TO SMO

Figure 6.10. National Surface Water Survey Form 3 - Shipping.

6.2.2.6 Turbidity - A Monitek Model 21 laboratory nephelometer is used to determine the turbidity of routine, duplicate, audit, and blank samples. Results are recorded on Form 5. The QC procedures are discussed in Section 7. The QC procedures are discussed in Section 7.

6.2.2.7 Specific Conductance - A YSI Model 32 meter with YSI 3400 series probe is used to determine the specific conductance of routine, duplicate, audit, and blank samples. The QC procedures are discussed in Section 7.

6.2.2.8 Sample Shipment - When a batch is completely processed and is ready for shipment, the samples are assembled into groups according to the analytical laboratory to which they are being shipped.

6.2.2.9 Data Distribution - Copies of all forms (except labels and Form 3) are kept at the mobile processing laboratory. Copies of Forms 3, 4, 4A, 5, 6, and 7 are sent to the locations indicated in Figure 6.11. One copy of Form 3 is sent to the Sample Management Office (SMO) and two copies are sent with the samples to the analytical laboratory. Upon receipt by the analytical laboratory, the condition of the samples is noted on the two forms and one form is forwarded immediately to SMO.

After the laboratory analyses are completed, the results are entered on the data reporting forms (see Appendix A) and are sent to the data base manager for entry into the data base. In either case, a copy of the results is sent to the QA staff for data evaluation. (Data evaluation is discussed in Section 13). QA for the data in the data base is discussed in Section 12.

6.3 Training

Prior to the NSS field activities, all personnel must be trained. Safety procedures and regulations, field operations, and mobile processing laboratory analytical procedures are the chief subjects of instruction. Training includes classroom instruction and realistic simulations of actual activities to be performed. Where possible, these simulations include sampling at a stream site and sample preparations in a mobile processing laboratory.

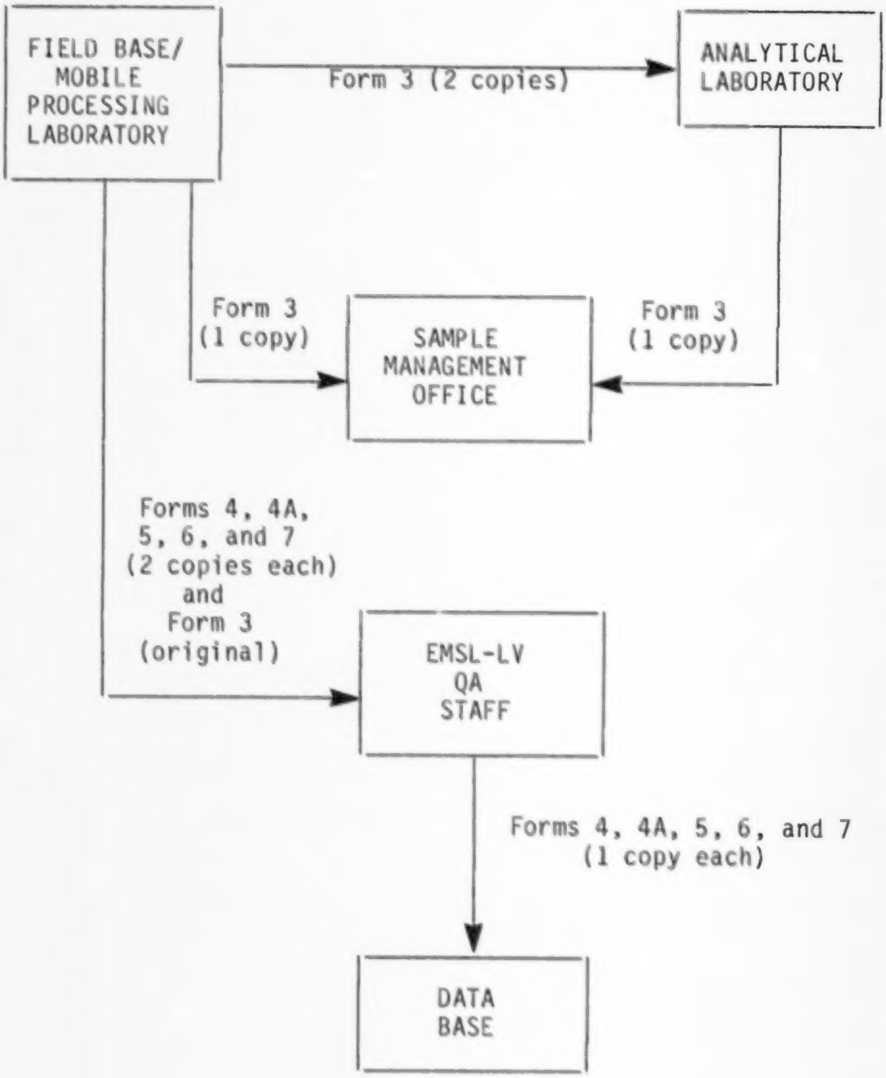
FIELD BASE/ MOBILE PROCESSING LABORATORY
Form 3 (2 copies)
ANALYTICAL LABORATORY
Form 3 (1 copy)
SAMPLE MANAGEMENT OFFICE
Form 3 (1 copy)
Forms 4, 4A, 5, 6, and 7 (2 copies each) and Form 3 (original)
EMSL-LV QA STAFF
Forms 4, 4A, 5, 6, and 7 (1 copy each)
DATA BASE

Figure 6.11. Flow scheme for field data forms.

7.0 FIELD MEASUREMENT QUALITY CONTROL CHECKS

Every sampling day, the sampling teams check the calibration of the meters used in the field. The check is performed at the field base prior to departure for sampling and again at the stream sites before and after stream measurements are taken. The mobile processing laboratory personnel conduct QC checks of their instruments after the samples are received at the mobile processing laboratory. The QC measurements are described in Sections 7.1 and 7.2.

7.1 Stream Site Measurements

Stream site measurements consist of six determinations. Five of these, stream temperature, pH, specific conductance, DO, and staff gauge height, are recorded on NSWS Stream Data Form 4. Flow velocity is recorded on the Hydrology Form (4A).

7.1.1 Site Measurements of Chemical Parameters - Portable pH, specific conductance, DO, and flow velocity meters are utilized in stream site measurements.

The QC procedures consist of calibration or calibration checks of the instruments before and after each sampling trip and of determining any change in instrument response between calibrations. These procedures are described in detail in Hagley et al. (1986). The following is a summary of the stream QC procedures.

Water temperature - Sample temperature readings are required in order to calculate temperature-corrected values for pH, specific conductance, and DO. Each meter has its own temperature function, which is checked every morning against an NBS-traceable thermometer. The readings must agree within 0.5°C. There is no calibration control for temperature, so the probe must be replaced if manufacturer's troubleshooting instructions do not resolve a discrepancy in the readings. All data taken with the defective probe must be qualified. The stream temperature obtained using the conductance meter is recorded on Form 4 as the in situ temperature, unless the meter temperature function was not within the acceptable criteria. In that case, the DO stream temperature is recorded, and a notation is made on Form 4.

pH - At each stream site, a QCCS that has a theoretical pH value of 4.00 must be analyzed prior to and following the stream pH determinations. If any QCCS reading deviates from the theoretical pH by more than 0.1 pH unit, the instrument is recalibrated and the pH of the QCCS is measured again. If the reading still does not meet the specifications and no functioning back-up electrode or meter is available, the appropriate data qualifier (listed in Table 9.8) is recorded on the Stream Data Form 4.

Specific Conductance - The meter in use has no conductance calibration controls. Therefore, the operator must determine if the manufacturer-set conductance calibration is within specifications by measuring QCCSs of 718, 147, and 74 µS/cm during the daily presampling calibration check. The allowed error on the QCCS is ±72 µS/cm, ±15 µS/cm, and ±10 µS/cm, respectively. If the reading is not within these limits, the manufacturer's troubleshooting guide should be consulted, and the meter or probe should be replaced if necessary. Before and after the in situ specific conductance determinations, a QCCS of 74 µS/cm is analyzed. The measured QCCS must be within 10 µS/cm, or the data must be qualified. The QCCS data are recorded on Stream Data Form 4.

Dissolved O_2 - No QCCS is analyzed at the stream site because the meter is recalibrated at each base site. The QC check is as follows: After the dissolved oxygen meter is calibrated with water-saturated air, air-saturated water is measured. The readings must be within 0.5 mg/L of one another, or the appropriate data qualifier must be recorded on Stream Data Form 4. The QC check is performed at the field base before and after each day's sampling.

Stream Flow - The manufacturer-set calibration of the flow meter is checked daily by the sampling team before the team leaves the field base for sampling and again at streamside before entering the stream. The meter reading should be 10.0 ± 0.2 ft/sec. Once a week, the zero value on the meter is checked and adjusted; the reading should be 0.0 ± 0.1 ft/sec.

There are no QC checks for staff gauge measurements.

7.2 Mobile Processing Laboratory Measurements

Measurements made at the mobile processing laboratory include DIC, pH, turbidity, specific conductance, PCV aluminum, and true color. The data are recorded on Form 5. The QC procedures are described in detail in Hillman et al. (1986) and Chaloud et al. (in preparation). This section contains a summary of the QC procedures.

7.2.1 Dissolved Inorganic Carbon - DIC is measured in routine, duplicate, and field audit samples using the Dohrman Model DC-80 carbon analyzer. The measurement procedure is as follows:

1. Initial calibration is performed using the working standard (10.00 mg/L C).

2. Two QC standards (2.00 mg/L C and 20.00 mg/L C) are measured to verify the initial calibration.

3. If both QC standards are within 10 percent of the theoretical concentration, the values are entered in the DIC logbook and analysis proceeds. If the standards are not within 10 percent, steps 1 and 2 are repeated.

4. A calibration blank is measured.

5. If the calibration blank is less than 0.1 mg/L C, the value is recorded and sample analysis continues. If the calibration blank is 0.1 mg/L C or greater, the laboratory supervisor is informed, corrective action is taken, and steps 1 through 5 are repeated. Normally, one calibration blank is analyzed at the beginning of the batch.

6. DIC is measured for eight samples.

7. A 2.0 mg/L C QCCS is analyzed to check the calibration.

8. If the QCCS is within 10 percent of the theoretical concentration, the value is recorded in the logbook and sample analysis continues. If the QCCS is not within 10 percent, it should be determined whether there is enough left of the samples associated with the unacceptable QCCS to reanalyze them. If enough sample is left, steps 1 through 7 are repeated, including analysis of all samples since the last acceptable QCCS. If not enough sample remains, the unacceptable QCCS value is recorded in the DIC logbook, the sample ID numbers associated with the unacceptable QCCS are noted, and the appropriate data qualifier is entered on Form 5 for the affected samples. Sample analysis must not continue until acceptable QCCS values are obtained.

9. One sample is measured in duplicate per batch. These duplicates are called trailer duplicates. If the difference between the two measurements is greater than 10 percent, another sample is analyzed in duplicate. If the difference is still greater than 10 percent, the laboratory supervisor is notified, and the problem is noted on Form 5 with a data qualifier.

10. When sample analysis is complete, a final QC check is required, and the relevant QC information is recorded on Form 5, Batch QC Field Data.

7.2.2 pH - pH is determined in routine, duplicate, and field audit samples using an Orion Model 611 pH meter with Orion Ross Model 8104 glass body combination pH electrode. The measurement procedure is as follows:

1. The instrument is standardized according to the manufacturer's instructions and the methods manual (Hillman et al., 1986).

2. The pH of pH 4 and pH 7 buffers is measured and the results are recorded in the logbook. If either measurement differs from the certified value by more than 0.02 pH units, steps 1 and 2 are repeated. If acceptable results cannot be obtained, the electrode is replaced and the above procedure is repeated. (Failed electrodes should be sent with a description of the problems observed to the QA manager at EMSL-LV where they will be tested further.)

3. When satisfactory results are obtained for the buffers, the pH of a pH 4.00 QC sample is measured and the result is recorded in the logbook. If the reading differs from 4.00 by more than 0.1 pH unit, steps 1 and 2 are repeated, and the pH of a fresh QCCS is measured. If acceptable results are still not obtained, the laboratory manager should be consulted. Stream samples are not to be analyzed until an acceptable value for the QCCS has been obtained.

4. Samples are measured for pH. After every five samples, a pH 4.00 QC sample is measured and the result is recorded in the logbook. If the measured pH of the QC sample is 4.0 ± 0.1 pH units, measurement of samples proceeds.

5. If the QCCS is not acceptable, it should be determined whether there is a sufficient amount of sample remaining in any of the other three syringes to repeat the analysis. If so, steps 1 through 3 are repeated and all samples analyzed since the last acceptable QCCS are reanalyzed. If not enough sample remains, the sample ID numbers associated with the unacceptable QCCS are recorded in the logbook.

6. One sample per batch is measured in duplicate. If the difference between the two measurements is greater than 0.1 pH unit, another sample is measured in duplicate. If the difference is still greater than 0.1 pH unit, the laboratory supervisor is notified, and the problem is noted on Form 5 with a data qualifier.

7. After the last sample in a batch has been analyzed, a final QCCS is analyzed and the value is recorded in the logbook.

8. When this analysis is completed, the relevant QC information is recorded on Form 5.

7.2.3 Turbidity - Turbidity is determined in routine, duplicate, field audit, trailer duplicate, and blank samples using the Monitek Model 21 laboratory nephelometer. The measurement procedure is as follows:

1. The nephelometer, set on Range 20, is zeroed and then is calibrated with a 10.0 NTU standard, following the manufacturer's recommendations.

2. Calibration linearity is verified by analyzing 2.0, 5.0, and 20.0 NTU QC samples. (The 20.0 NTU QC sample is measured on Range 200.) The measured values must be 2.0 ± 0.2, 5.0 ± 0.5, and 20.0 ± 2.0. If the measured values are unacceptable, step 1 is repeated. Acceptable results must be obtained prior to sample analysis. Acceptable results for the 5.0 NTU QC sample are recorded on Form 5.

3. For every eight samples, a 5.0 NTU QC sample is measured. If the measured value is 5.0 ± 0.5 NTU, QC and sample results are recorded on Form 5.

4. If the QC measurement is unacceptable, the instrument must be recalibrated and the previous eight samples must be reanalyzed. Acceptable QC values are recorded on Form 5 along with associated sample results.

   Note: Some samples must be analyzed on range 2 or on range 200. If the range 200 setting is used, the instrument must be recalibrated and a different QCCS must be analyzed.

7.2.4 True Color - The only QC check on true color is that one sample per batch is measured in duplicate. If the two measurements differ by more than 10 units, another sample is measured in duplicate. If acceptable results are still not obtained, the laboratory supervisor must be notified and a data qualifier must be recorded on Form 5 with the results. Acceptable results are also recorded on Form 5.

7.2.5 Nonexchangeable and Total PCV-Reactive Aluminum - Nonexchangeable and total PCV-reactive aluminum is determined in routine, duplicate, audit, blank, and trailer duplicate samples using a Lachat FIA. The measurement procedure is as follows:

1. Three calibration ranges may be defined. For the low range, 0, 10, 25, 50, 65, 100, and 125 ppb calibration standards are used; for the high range, 750, 1250, 1750, 2250, and 3000 ppb calibration standards are used; and for samples with very high levels of analyte, a calibration range is defined by standards with concentrations of 1000, 2000, 3000, and 5000 ppb.

2. After every 10 samples, a 75 ppb QCCS is analyzed. The measured value of the QCCS must be 75 ppb ±10 percent for channel 1, and 75 ppb ±20 percent for channel 2.

3. If the QCCS measurement is unacceptable, the instrument must be recalibrated and the previous 10 samples must be reanalyzed. Acceptable QC values are recorded on Form 5.

7.2.6 Specific Conductance - Specific conductance is measured for routine, duplicate, audit, blank, and trailer duplicate samples using a YSI conductance meter and probe. The measurement procedure is as follows:

1. A calibration blank and a 147 µS/cm calibration standard are measured and the cell constant is calculated.

2. After every 10 samples, QCCS of 14.7, 72.8 and 147 µS/cm are measured. The QCCSs are prepared from a different stock solution than are the calibration standards.

3. If the QCCS measurements are unacceptable, the instrument must be recalibrated and the previous 10 samples must be reanalyzed. Acceptable values for the 147 µS/cm QCCS are recorded on Form 5.

4. A final 147 µS/cm calibration standard is measured and the cell constant is recalculated.

5. The temperature is recorded in the logbook. Values on Form 5 are corrected for the cell constant but not for temperature (25°C). The temperature log is photocopied and the copy is attached to Form 5 so that temperature corrections can be performed by EMSL-LV QA staff.

8.0 ANALYTICAL PROCEDURES

Table 8.1 lists the analytical procedures that are used to determine each required parameter. A detailed description of these procedures is provided in the methods manual (Hillman et al., 1986). Internal QC checks on the analytical procedures are discussed in the next section.

TABLE 8.1. PARAMETERS AND CORRESPONDING MEASUREMENT METHODS

Parameter	Method[a]
1. ANC	Titration with Gran plot
2. BNC	Titration with Gran plot
3. Aluminum, total	EPA Method 202.2 AAS (furnace)
4. Aluminum, total extractable	Extraction with 8-hydroxyquinoline into MIBK followed by AAS (furnace)
5. Aluminum, Nonexchangeable and total PCV reactive[b]	Automated colorimetric pyrocatechol violet (PCV)[c]
6. Ammonium, dissolved	EPA Method 350.1
7. Calcium, dissolved	EPA Method 215.1 - AAS (flame)
8 Chloride, dissolved	Ion chromatography
9. Fluoride, total dissolved	Ion selective electrode
10. Inorganic carbon, dissolved	Instrumental (Similar to DOC)
11. Iron, dissolved	EPA Method 236.1 - AAS (furnace)
12. Magnesium, dissolved	EPA Method 242.1 - AAS (flame)
13. Manganese, dissolved	EPA Method 243.1 - AAS (flame)
14. Nitrate, dissolved	Ion chromatography
15. Organic carbon, dissolved	EPA Method 415.2
16. pH	pH electrode and meter
17. Phosphorus, total dissolved[d]	USGS Method I-4600-78 or Modified USGS Method
18. Potassium, dissolved	EPA Method 258.1 - AAS (flame)
19. Silica, dissolved	USGS Method I-2700-78
20. Sodium, dissolved	EPA Method 273.1 - AAS (flame)
21. Sulfate, dissolved	Ion chromatography
22. Specific conductance	EPA Method 120.1

[a] AAS methods are taken from U.S. EPA, 1983. Laboratories that have ICP instrumentation may use EPA Method 200.7, reproduced in Appendix A of Hillman et al. (1986), for determining Ca, Fe, Mg, and Mn, providing they can demonstrate the detection limits specified in Table 4.1. If the ICP instrumentation cannot meet the required detection limits, it may still be used to analyze samples which contain the analytes at concentrations greater than 10 times the ICP detection limit. Other samples must be analyzed by furnace or flame AAS.

[b] Determined in the mobile processing laboratory.

[c] Nonexchangeable and total PCV reactive aluminum extraction was not performed for the Phase I - Pilot Survey but is performed for the other three surveys.

[d] For the Pilot Survey, total P was determined (samples were unfiltered). For the Mid-Atlantic - Phase I, Southeast Screening, and Episodes Pilot Surveys, total dissolved P was determined (samples were filtered).

9.0 ANALYTICAL INTERNAL QUALITY CONTROL

9.1 Sample Receipt

All samples received by the analytical laboratory should be checked in by a receiving clerk who (1) records the date received on the shipping form, (2) checks the samples to identify discrepancies with the shipping form, (3) fills out the "sample condition" portion of the shipping form, and (4) mails a copy of the completed shipping form to SMO. The "sample condition" column should note such information as leakage in shipping, insufficient sample, noticeable suspended particulates, partially frozen samples, and the temperature of the sample containers. If there are any discrepancies, the field base coordinator must be notified immediately. These data are kept on a computer file by SMO and are available to interested parties. The laboratory retains a copy of the completed shipping form for the laboratory records. The samples are refrigerated as soon as possible.

Samples are received already preserved and ready for analysis. Sample aliquots 2, 3, 4, 5, 6, and 8 are stored at 4°C in the dark while not in use. When an analysis is to be performed, the analyst should remove an aliquot from the sample and should return the sample to the refrigerator as soon as possible.

Even after all analyses have been completed and the results have been checked, samples remain stored in a refrigerator at 4°C for 6 to 12 months, or until laboratory personnel are notified otherwise by the QA manager, in case reanalysis is necessary.

9.2 Sample Analysis

Procedures given in the methods manual (Hillman et al., 1986) are to be followed exactly. Table 8.1 is a list of all required measurements and the associated methods. Table 4.1 lists the required precision, expected ranges, and detection limits for each parameter. All analyses for each parameter must be performed within the specified holding times given in Table 9.1.

9.3 Analytical Laboratory Documentation for Quality Control

The following documents and information must be updated constantly and must be available to the analyst and to the supervisor involved in the project:

- laboratory standard operational procedures (SOPs) - detailed instructions about the laboratory and instrument operations.

TABLE 9.1. MAXIMUM HOLDING TIMES

Holding Time	7 days	14 days	28 days	28 days[a]
Parameter	NO_3^-[b]	ANC	Total P	Ca
		BNC	NH_4^+	Mg
	Total extractable and organic extractable Al	DIC, initial and equilibrated	SO_4^{2-}	Na
		DOC	F^-	Total Al
		pH[c]	SiO_2	Mn
				Fe
		Specific Conductance	Cl^-	K

[a] Although the EPA (U.S. EPA, 1983) recommends a 6-month holding time for these metals, this study requires that all of the metals be determined within 28 days. This requirement ensures that significant changes do not occur and that data are obtained in a timely manner.

[b] Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (un-acidified) be determined within 48 hours of collection, evidence exists (Peden, 1981 and APHA et al., 1985) that nitrate is stable for 2 to 4 weeks if stored in the dark at 4°C.

[c] Although the EPA (U.S. EPA, 1983) recommends that pH be measured immediately after sample collection, evidence exists (McQuaker et al., 1983) that it is stable for as long as 15 days if stored at 4°C and sealed from the atmosphere. The pH is also measured in a sealed sample at the mobile processing laboratory within 48 hours of sample collection.

- laboratory QA plan - clearly defined laboratory protocol, including personnel responsibilities and use of QC samples.
- list of in-house samples - including projected dates for completion of analyses; allows analyst to schedule further analyses.
- instrument performance study information - information on baseline noise, calibration standard response, precision as a function of concentration, and detection limits; used by analyst and supervisor to evaluate daily instrument performance.
- QC charts - the most recent QC charts with 99 percent and 95 percent control limits for all QCCS and detection limit QCCS, generated and updated for each batch. The same QCCS must be used for all QC charts to ensure the continuity of the charts. (Note: The purpose of preparing QCCS charts is to ensure that the actual control limits do not exceed the limits given in Table 9.2.)
- data sheet QC report - report by the laboratory manager reviewing QC results for each parameter and flagging all results outside statistically established QC limits for reanalysis before data are submitted to recipients.

9.4 Internal Quality Control Within Each Method

Internal QC must be an integral part of any measurement procedure to ensure that results are reliable. Internal QC procedures for each method are summarized in Table 9.3. These QC procedures are performed for every sample batch, unless otherwise noted. QC procedures for certain measurements (pH, BNC, ANC, and specific conductance) are detailed in the appropriate method description in Hillman et al. (1986). Details on internal QC procedures for automated colorimetric analyses (total or total dissolved P, NH_4^+ and SiO_2), instrumental carbon analyses (DIC and DOC), ion-selective electrode analysis (F^-), ion chromatography analyses (NO_3^-, Cl^-, and SO_4^{2-}), and atomic absorption or emission analyses (Ca, Mg, K, Na, Mn, Fe, total Al, and total extractable Al) are described below.

1. Initial Calibration - An initial calibration is performed as required for each analytical method. Next, the linear dynamic range (LDR) is determined for the initial calibration. The concentrations of the calibration standards must bracket the expected sample concentrations. (Occasionally the standards suggested by a method must be adjusted to meet this requirement.) The low standard should not be greater than 10 times the detection limit. If during the analysis the concentration of a sample is above the LDR, two options are available. One option is to dilute and reanalyze the sample. In this case, the diluent should have a matrix similar to the sample matrix with respect to all preservatives (acid type and concentration) used. Alternatively,

TABLE 9.2. MAXIMUM CONTROL LIMITS FOR QUALITY CONTROL CHECK SAMPLES

Parameter	Maximum Control Limit for QCCS (% Deviation from Theoretical Concentration of QCCS)
Al, Nonexchangeable and total PCV reactive	±20%
Al, total extractable	±20%
Al, total	±20%
Ca	±5%
Cl^-	±5%
DIC	±10%
DOC	±10%
F^-, total dissolved	±5%
Fe	±10%
K	±5%
Mg	±5%
Mn	±10%
Na	±5%
NH_4^+	±10%
NO_3^-	±10%
P, total dissolved	±20%
pH	±0.05 pH unit
SiO_2	±5%
SO_4^{2-}	±5%
Specific Conductance	±2%

TABLE 9.3. SUMMARY OF INTERNAL QUALITY CONTROL CHECKS FOR ANALYSIS METHODS

Parameter or Method	QC Check	Control Limits	Corrective Action[a]
ANC, BNC, pH	1. Titrant standardization crosscheck	1. Relative differences <5%	1. Restandardize titrants.
	2. Electrode calibration (Nernstian response check)	2. Slope = 1.00 ± 0.05	2. Recalibrate or replace electrode.
	3. pH QCCS (pH 4 and 10) analysis	3. pH 4 = 4.00 ± 0.05 pH 10 = 10.00 ± 0.05	3. Recalibrate electrode.
	4. Blank analysis (salt spike)	4. |Blank| $\leq$10 μeq/L	4. Prepare fresh KCl spike solution.
	5. Duplicate analysis	5. RSD <10% (ANC and BNC) ± 0.05 pH units (pH)	5. Refine analytical technique, analyze another duplicate.
	6. Protolyte comparison	6. See Section 13.2.4	6. See Section 13.2.4
Ions (Cl^-, total dissolved F^-, NH_4^+, NO_3^-, SO_4^{2-})	1a. Initial QCCS analysis (calibration and verification)	1a,b. The lesser of the 99% CI or value given in Table 9.2	1a. Prepare new standards and recalibrate.
Metals (total Al, total extractable Al, Ca, Fe, K, Mg, Mn, Na)	1b. Continuing QCCS analysis (every 10 samples)		1b. Recalibrate. Reanalyze associated samples.
	2a. Detection limit determination (weekly)	2a. Detection limits given in Table 4.1	2a,b. Optimize instrumentation and technique.
SiO_2, total or total dissolved P, DIC, DOC, spec. cond.	2b. DL QCCS analysis (daily; for the parameters designated in Section 9.4	2b. % Recovery = 100 ± 20%	
	3. Blank analysis	3a. Blank $\leq$2 x DL (except sp. cond.) 3b. Blank $\leq$0.9 μS/cm (sp. cond. only)	3a,b. Determine and eliminate contamination source. Prepare fresh blank solution. Reanalyze associated samples.
	4. Duplicate analysis	4. Duplicate precision (%RSD) limits given in Table 4.1	4. Investigate and eliminate source of imprecision. Analyze another duplicate.

(continued)

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[a] To be followed when QC check is outside control limits.

TABLE 9.3. (Continued)

Parameter or Method	QC Check	Control Limits	Corrective Action[a]
Ions (Cl^-, total dissolved F^-, NH_4^+, NO_3^-, SO_4^{2-}) Metals (total Al, total extractable Al, Ca, Fe, K, Mg, Mn, Na) SiO_2, total or total dissolved P, DIC, DOC, spec. cond.	5. Matrix spike[b] (except ext. Al, DIC, and spec. cond.)	5. % Recovery = 100 ± 15%	5. Analyze 2 additional spikes If one or both outside control limits, analyze all samples in that batch by method of standard additions.
	6. Resolution test (IC only)	6. Resolution $\geq$60%	6. Clean or replace separator column. Recalibrate.

[a] To be followed when QC check is outside control limits.
[b] Matrix spikes were performed for the Phase I - Pilot Survey only.

two concentration ranges may be calibrated. Samples are first analyzed on the lower concentration range. Each sample whose concentration exceeds the upper end of the LDR is then reanalyzed on the higher concentration range. If this option is taken, separate QC samples must be analyzed and reported for each range.

2. QCCS - Immediately after the instruments are standardized, a QCCS containing the analyte of interest at a concentration in the mid-calibration range must be analyzed. If a wider range than necessary is calibrated (e.g., for analysis by inductively coupled plasma emission spectroscopy), the QC sample must be in the same concentration range as the samples. QCCS may be obtained commercially or may be prepared by the analyst from a source which is independent from the calibration standards (i.e., the QCCS cannot be made by diluting the same stock solution used to make the calibration standards). The calibration QC sample must be analyzed to verify the calibration curve prior to any sample analysis, after every 10 samples, and after the last sample. The observed value for the QC sample must not differ from the theoretical value by more than the limits given in Table 9.2. When an unacceptable value for the calibration QC sample is obtained, the instrument must be recalibrated and all samples that were analyzed after the last acceptable QC sample must be reanalyzed. Furthermore, the observed concentrations for the QC sample must be plotted on a QC chart and 99 percent and 95 percent confidence intervals must be developed. To ensure the continuity of QC charts, a QCCS sample of the same theoretical concentration must be used throughout the plotting process. The 99 percent control limit must not differ from the theoretical value by more than the limits given in Table 9.2. If it does, the QA manager must be consulted. Weekly, QC charts should be updated, cumulative means should be calculated, and new warning and control limits (95 percent and 99 percent, respectively) should be determined. To indicate bias for a given analysis, there must be at least seven successive points on one side of the theoretical mean. If bias is indicated, analysis must be stopped and an explanation must be sought.

3. Detection Limit QCCS - This is a low-level QC sample that contains the analyte of interest at a concentration two to three times the required detection limit. This QC sample must be analyzed once per batch for the following parameters: total extractable Al, total Al, dissolved metals (Ca, Fe, K, Mg, Mn, Na), anions (Cl^-, SO_4^{2-}, NO_3^-), NH_4^+, SiO_2, DOC, air-equilibrated DIC, initial DIC, and total or total dissolved P. The results are reported on Form 20, Blanks and QCCS Results (see Table 9.4.). The purpose of the detection limit QC sample is to eliminate the necessity of formally determining the detection limit on a daily basis. The measured value must be within 20

TABLE 9.4. DATA FORMS USED BY THE ANALYTICAL LABORATORY[a]

Data Form	Description
11	Summary of Sample Results
13	ANC and BNC Analyses Results
14[b]	QC Data for ANC and BNC Analyses
15[b]	Specific Conductance (Measured and Calculated)
16[b]	Anion-Cation Balance Calculations
17	Ion Chromatography Resolution Test
18	Detection Limits
19	Sample Holding Time Summary
20	Blanks and QCCS Results
21[b]	Dilution Factors
22	Duplicates Results

[a] These forms are shown in Appendix A.

[b] Form not required to be submitted with data package but recommended for internal QC requirements.

percent of the theoretical concentration. If it is not, the problem must be identified and corrected, and an acceptable result must be obtained prior to sample analysis.

4. Calibration Blank - A calibration blank must be analyzed once per batch, immediately after the initial calibration, to check for baseline drift and low-level calibration-curve bias (y-intercept). Rezero if necessary. The calibration blank is defined as a "0" mg/L standard and contains only the matrix of the calibration standards. The observed concentration of the calibration blank must be less than or equal to twice the required detection limit. If it is not, the instrument must be rezeroed and the calibration must be rechecked.

5. Reagent Blank - A reagent blank must be prepared and analyzed for each batch of samples for methods which require sample preparation (dissolved SiO_2 and total Al). A reagent blank is defined as a sample composed of all the reagents (in the same quantities) used in preparing a real sample for analysis. It is also carried through the same digestion and extraction procedure as a real sample. The concentration of the reagent blank must be less than or equal to twice the required detection limit. If the concentration exceeds this limit, the source of contamination must be investigated and eliminated. A new reagent blank must be prepared and analyzed for each sample in which the high reagent blank value contributed significantly (>10 percent) to the value of the parameter in question. If a high reagent blank problem cannot be corrected, the QA manager must be contacted. Reagent blank results are reported on Form 20 but are not subtracted from sample results.

6. Preliminary Sample Analysis - Approximately seven samples and a reagent blank must be analyzed prior to duplicate analyses to determine approximate endogenous sample concentrations.

7. Duplicate Sample Analysis - One sample per batch must be prepared and analyzed in duplicate for each parameter. The relative standard deviation is plotted on a QC chart and 99 percent and 95 percent confidence intervals are established. Initial control limits are set at the precision levels given in Table 4.1. The control limits should not exceed these values. If they do, the QA manager must be notified immediately. If duplicate values fall outside the control limits, an explanation must be sought (such as instrument malfunction, calibration drift, etc.). A second, different sample must then be analyzed in duplicate. No further samples may be analyzed until duplicate sample results are within the control limits, unless approval is given

by the QA manager. The percent relative standard deviation (%RSD) is calculated as described below:

$$\%RSD = \frac{s}{\overline{X}} \times 100$$

$$s = \left(\frac{\Sigma(\overline{X} - X)^2}{n - 1}\right)^{1/2}$$

where: s is the standard deviation

$\overline{X}$ is the mean

n is the routine (or other sample)/duplicate pair (=2)

8. Matrix Spike Analysis - Matrix spike analysis was performed ONLY for the Phase I - Pilot Survey. A matrix spike was not required for total extractable Al analyses. The procedure used is as follows: One matrix spike is prepared for each batch by spiking an aliquot of a sample* with a known quantity of analyte prior to analysis. The spike concentration must be twice the endogenous level or 10 times the required detection limit, whichever is larger. Also, the volume of the spike added must be negligible (less than or equal to 1 percent of the sample aliquot volume). The spike recovery must be 100 ± 15 percent to be acceptable. If the recovery is not acceptable for all parameters, two additional, different samples must be spiked with the analyte in question, must then be analyzed, and recoveries must be calculated. If one or both recoveries are not 100 ± 15 percent, the entire batch must be analyzed by standard additions for the parameter in question. The standard addition is performed by analyzing the sample, the sample plus a spike at about the endogenous level, and the sample plus a spike at about twice the endogenous level. The concentration of the matrix spike must not exceed the linear range of the method. For this reason, the matrix spike for graphite furnace analyses, which determine low levels of analyte, must be chosen judiciously and may be different than suggested above. The samples may be diluted or the spike levels may be adjusted so that the linear range is not exceeded when performing

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*QA analysis on a full sample is recommended. If sufficient sample volume is not available, QA analysis may be performed on a per-aliquot basis.

standard additions for furnace AA analyses. The percent recovery of spikes is calculated as described below:

$$\%\text{ spike recovery} = \frac{\text{value of sample plus spike} - \text{value of unspiked sample}}{\text{value of spike added}} \times 100$$

9. Ion Chromatography Resolution Test - An ion chromatography resolution test must be performed once per analytical run (day) by analyzing a standard that contains approximately equal concentrations of nitrate and sulfate ions (1 mg/L). If the resolution does not exceed 60 percent, the column should be replaced and the resolution test should be repeated.

10. Continuing Sample Analysis - The remaining samples are analyzed if the reagent blank, duplicate, and QC samples are within limits. After every 10 (or fewer) samples and after the last sample, a QC sample must be analyzed to continually verify the calibration curve. If the measured value differs from the theoretical value by more than the limits given in Table 9.2, the instrument is recalibrated and the previous 10 samples are reanalyzed.

9.5 Overall Internal Quality Control

Once the value of each parameter in a sample is determined, there are several procedures for checking the correctness of analyses. These procedures are outlined in the following subsections.

9.5.1 Anion-Cation Balance - Theoretically, the ANC of a sample equals the difference, expressed as microequivalents per liter (μeq/L), between the concentration of cations and the concentration of anions in a sample (Kramer, 1982). In practice, this is rarely the case; deviations are caused by analytical variability and the presence of ions (protolytes) that are not measured (e.g., organic ions). The concentrations of these unmeasured ions can be significant in natural lake samples. The percent ion difference (%ID) calculation below utilizes the ANC value to take these ions into account; as a result, the calculation is more accurate. For each sample, %ID is calculated as follows:

$$\%ID = \frac{ANC + \Sigma\text{ anions} - \Sigma\text{ cations}}{TI} \times 100$$

where:

$$\Sigma\text{ anions} = [Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}]$$

$$\Sigma \text{ cations} = [Na^{+}] + [K^{+}] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^{+}]$$

$$TI = \text{total ion strength} = ANC + \Sigma \text{ anions} + \Sigma \text{ cations} + 2[H^{+}]$$

$$ANC = [HCO_3^{-}] + 2[CO_3^{2-}] + [OH^{-}] + [\text{titrated organic bases}] - [H^{+}]$$

$$[H^{+}] = (10^{-pH}) \times 10^{6} \ \mu eq/L$$

All concentrations are expressed as microequivalents per liter. A list of factors for converting mg/L to µeq/L for each parameter is given in the methods manual (Hillman et al., 1986). Samples which have a poor ion balance are reanalyzed. Table 9.5 lists the criteria for reanalysis.

Prior to reanalysis, the data should be checked for possible causes of poor ion balance. This check may indicate which analytical results give rise to poor ion balance and, hence, the parameters for which the sample should be reanalyzed. Also, careful examination of the data may explain the poor ion balance. For example, if the %ID is negative and the DOC is large enough to account for the difference, unmeasured organic anions are probably responsible; thus, reanalysis is unnecessary. The QA manager must be contacted when questions arise regarding reanalysis.

9.5.2 Conductance Balance - An approximation of the conductance of a sample can be calculated by adding together the equivalent conductances for each measured ion at infinite dilution. The calculated conductances are determined by multiplying the concentration of each ion by the appropriate factor given in Table 9.6. The percent conductance difference (%CD) is calculated as follows:

$$\%CD = \frac{\text{calculated cond.} - \text{measured cond.}}{\text{measured conductance}} \times 100$$

Samples which have %CDs that exceed the limits listed in Table 9.5 are reanalyzed. As with the %ID calculation, an unacceptable value for %CD indicates either the presence of unmeasured ions or an analytical error in the measurement. For the surface waters sampled, the ions included in the %CD calculation are expected to account for 90 to 100 percent of the ions in a sample. However, in contrast to the percent ion difference calculation, there is no term in the %CD calculation to account for protolytes that are not specifically determined. The QA manager must be contacted when questions arise regarding reanalysis.

9.6 Instrumental Detection Limits

Instrumental Detection Limits (IDLs) must be determined and reported weekly for each parameter except pH, specific conductance, ANC, and BNC. For this study, the IDL is defined as three times the standard deviation

TABLE 9.5. CHEMICAL REANALYSIS CRITERIA

A. Anion-Cation Balance

Total Ion Strength (µeq/L)	% Ion Maximum Balance Difference[a]
<50	60
≥50 <100	30
≥100	15

B. Specific Conductance

Measured Specific Conductance (µS/cm)	Maximum % Specific Conductance Difference[a]
<5	50
≥5 <30	30
≥30	20

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[a] If the absolute value of the percent difference exceeds these values, the sample is reanalyzed. When reanalysis is indicated, the data for each parameter are examined for possible analytical error. Suspect results are then redetermined and the above percent differences are recalculated (Peden, 1981). If the percent differences for reanalyzed samples are still unacceptable or no suspect data are identified, the QA manager must be contacted for guidance.

TABLE 9.6. CONDUCTANCE FACTORS OF IONS[a,b]

Ion	Specific Conductance (µS/cm at 25°C) per mg/L	Ion	Specific Conductance (µS/cm at 25°C) per mg/L
Ca^{2+}	2.60	Na^{+}	2.13
Cl^{-}	2.14	NH_4^{+}	4.13
CO_3^{2-}	2.82	SO_4^{2-}	1.54
H^{+}	3.5×10^{5} (per mole/L)	NO_3^{-}	1.15
HCO_3^{-}	0.715	K^{+}	1.84
Mg^{2+}	3.82	OH^{-}	1.92×10^{5} (per mole/L)

$$[H^+] \text{ moles/L} = 10^{-pH}$$

pH = initial pH measured before acidity titration.

$$[OH^-] = \frac{Kw}{[H^+]}$$

$$HCO_3^- = \frac{5.080\ [DIC(mg/L)]\ [H^+]\ K_1}{[H^+]^2 + [H^+]\ K_1 + K_1K_2}$$

$$CO_3^{2-} = \frac{4.996\ [DIC(mg/L)]\ K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$$

$K_1 = 4.4463 \times 10^{-7}$ $K_2 = 4.6881 \times 10^{-11}$ $K_W = 10^{-13.80}$

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[a] Taken from American Public Health Association et al. (1985), and from Weast (1972).

[b] Conductance factors are not given for ionic aluminum, iron, or manganese because these ions are rarely present in concentrations great enough to affect the percent conductance difference.

of 10 nonconsecutive replicate reagent or calibration blank analyses. Calibration blanks are analyzed when a method does not require a reagent blank. In some analyses, such as those using ion chromatography and Technicon AutoAnalyzers, a signal may or may not be obtained for a blank analysis. If a signal is not obtained for a blank analysis, the IDL is defined as three times the standard deviation of 10 nonconsecutive replicate analyses of a standard whose concentration is three to four times the required detection limit. Detection limits must not exceed the limits listed in Table 4.1.

9.7 Data Reporting

Results from each method are recorded on the appropriate data forms (Table 9.4). After a sample (all aliquots) is completely analyzed, the results are summarized on Form 11 (Summary of Sample Results) and are reported to the number of decimal places listed in Table 9.7. Results are annotated by the data qualifiers (tags) listed in Table 9.8, where applicable. After a form is completed, the analytical laboratory supervisor must sign it to indicate that he or she has reviewed the data and that the samples were analyzed exactly as described in the methods manual (Hillman et al., 1986). All deviations from the manual require the authorization of the QA manager prior to sample analysis.

Copies of raw data must be submitted as requested by the QA manager. All original raw data must be retained by the lab until notified otherwise by the QA manager. Raw data include data system printouts, chromatograms, notebooks, QC charts, standard preparation data, and all information pertinent to sample analysis.

9.8 Daily Evaluation of Quality Control Data

Each laboratory should make a daily sample status report by telephone to the EMSL-LV QA staff as directed. The objective of these reports is to keep the QA manager informed of the status of the internal and external QC checks in the laboratory in order to identify and solve problems that may arise. The reports also allow the QA manager to obtain preliminary results for the blanks, duplicates, and laboratory and field audit samples that are double-blind to the laboratories. (A discussion of blind and double-blind samples is presented in Section 10.) Otherwise, these data would not be available for QA/QC data evaluation until they were reported by the laboratories, which may be as long as 35 days after the samples are received. During the daily telephone contact, the EMSL-LV QA staff record all communications into a bound notebook to track and resolve all problems encountered during analyses.

Each week QC charts are updated and new control and warning limits are determined. The QA chemist then performs a QC audit in which all the data are reviewed. Any values that lie outside the control or warning limits are

TABLE 9.7. LIST OF DECIMAL PLACE REPORTING REQUIREMENTS

Parameter	Recommended Number of Decimal Places in Reported Results[a]
Al, total extractable	4
Al, total	4
ANC	1
BNC	1
Ca	3
Cl^-	3
DIC	3
DOC	2
F^-, total dissolved	4
Fe	3
K	3
Mg	3
Mn	3
Na	3
NH_4^+	3
NO_3^-	4
pH	2
P, total	4
SiO_2	3
SO_4^{2-}	3
Specific conductance	1

[a] Report to the number of decimal places in the actual IDL plus one.

TABLE 9.8. NATIONAL SURFACE WATER SURVEY LAB/FIELD DATA QUALIFIERS (TAGS)

Qualifier	Indicates
A	Instrument unstable
B	Redone, first reading not acceptable
C	Instruments, sampling gear not vertical in water column
D	Slow stabilization
E	Result not available; sample destroyed during shipment.
F	Result outside QA criteria (with consent of QA manager)
G	Atypical result; already reanalyzed and confirmed by the laboratory manager
H	Holding time exceeded criteria
J	Result not available; insufficient sample volume shipped to analytical laboratory from the mobile processing laboratory
K	Result not available; entire aliquot not shipped
L	Not analyzed because of interference
M	Result not available; sample lost or destroyed by lab
N	Not required
P	Result outside QA criteria, but insufficient volume for reanalysis
Q	Result outside QA criteria
R	Result from reanalysis
S	Contamination suspected
T	Leaking container
U	Result not required by procedure; unnecessary
V	% Ion Balance Difference (%IBD) value (Form 16) outside criteria because of high DOC
W	% Difference (%D) calculation for calculated ANC (Form 14) outside criteria because of high DOC
X, Y, Z	Available for miscellaneous comments in the field/mobile processing laboratory only

checked to verify that they are not the result of a transcription error. If bias is indicated (seven successive points on one side of the theoretical mean), analyses are stopped and an explanation is sought. Copies of the plots are given to the analytical laboratory supervisor, the QA chemist, and each analyst.

10.0 PERFORMANCE AND SYSTEM AUDITS

10.1 Performance Audit Samples

Field and laboratory audit samples are used as part of the QA activities for NSS. The audit samples are shipped to the analytical laboratories from the mobile processing laboratory as though they were routine stream samples. Every attempt is made to ensure that the analytical laboratory does not recognize the audit samples as different from the routine samples. As a result, the audit samples are double-blind to the analytical laboratory. That is, the laboratory neither recognizes them as audit samples nor knows their compositions.

10.1.1 Field Audit Samples - The purpose of field audit samples is to identify problems that affect data quality and that may occur during sample processing, shipment, or analysis. These problems could include sample contamination, sample degradation, solvent evaporation, and improper or inaccurate sample analysis. When used in conjunction with laboratory audit samples, the analysis of these samples provides data that can be used to distinguish mobile processing laboratory problems from analytical laboratory problems. There are two types of field audit samples: synthetic field audit samples and natural field audit samples.

The synthetic field audit samples are prepared at a central laboratory and are sent to the mobile processing laboratory to undergo all the filtration and preservation steps and to be labeled as though they were authentic stream samples. Thus, they are single-blind samples to the field laboratory (i.e., recognized as audit samples but of unknown composition) and, concurrently, double-blind samples to the analytical laboratory. The desired composition of the synthetic field audit samples is shown in Table 10.1.

Waters collected from Big Moose Lake in the Adirondack Mountains and Bagley Lake in the state of Washington are available to be utilized as natural audit samples for the survey. The waters of Big Moose Lake are low in alkalinity and thus are susceptible to acidic deposition; the Bagley Lake waters represent a medium level of alkalinity. These natural samples are passed through a 0.45µ filter and are maintained at 4°C to minimize changes in composition. Aliquots are prepared in the mobile processing laboratory from 2-liter portions of these waters and are included as part of a batch.

10.1.2 Laboratory Audit Samples - The purpose of these samples is to identify problems that affect data quality and that may occur during the analytical process. Thus, lab audit samples help verify the accuracy of analytical procedures and ensure that the laboratory continues to properly analyze samples.

TABLE 10.1. DESIRED COMPOSITION RANGE OF SYNTHETIC FIELD AND LABORATORY AUDIT SAMPLES FOR THE NATIONAL STREAM SURVEY

Parameter	Concentration Range	Units
ANC[a]	10-50	µeq/L
Al (total and total extractable)	0.01-0.10	mg/L
BNC[a]	10-50	µeq/L
Ca	0.1-1.0	mg/L
Cl^-	0.1-1.0	mg/L
DIC	0.1-1.0	mg/L
DOC	0.1-1.0	mg/L
F^-, total dissolved	0.01-0.05	mg/L
Fe	0.02-1.0	mg/L
K	0.1-1.0	mg/L
Mg	0.1-1.0	mg/L
Mn	0.02-1.0	mg/L
Na	0.5-3.0	mg/L
NH_4^+	0.01-0.50	mg/L
NO_3^-	0.01-0.50	mg/L
P, total dissolved	0.005-0.030	mg/L
pH[a]	4-5	pH
SiO_2	1-5	mg/L
SO_4^{2-}	1-5	mg/L
Specific Conductance[b]	1-50	µS/cm

[a] These parameters are related and affect the analytical results of one another.

[b] To be determined by concentration of other parameters.

Note: Mass balance (anions vs. cations) must be maintained.
Nitrogen/phosphorus ratio must be reasonable (10/20).

The synthetic laboratory audit samples are sent to the mobile processing laboratory from a central laboratory, already split into seven aliquots (eight aliquots for the Phase I - Pilot Survey). The audit samples are labeled by the mobile processing laboratory personnel, are included in a batch with routine stream samples processed on the same day, and are shipped to the analytical laboratory for analysis.

The desired composition of the synthetic laboratory audit samples is given in Table 10.1. Only low-concentration synthetic samples are used for NSS because the stream samples are not expected to contain analytes at higher levels.

10.1.3 Application of Audit Sample Data - Data are obtained from the analyses of the audit samples for the following purposes:

- to judge the performance of the mobile processing laboratory in the preparation and shipment of samples
- to judge the continued capability of the analytical laboratories to properly analyze the samples
- to establish a statistically valid estimate of the overall bias and precision of the analyses
- to establish a statistically valid estimate of the stability of a typical stream sample when stored at 4°C by evaluating the natural lake sample over the period of the study.

Acceptance windows are established for the measurement of each parameter in the audit samples. The size of the windows is based on the information available for each analytical method at the time the study is initiated. If the analytical results for a measurement fall outside the acceptance window, the EMSL-LV QA staff reviews the data to determine the cause of the problem and immediately contacts the analytical laboratory, mobile processing laboratory, or field base, whichever is appropriate, to seek corrective action. Data for routine samples analyzed with the audit samples are also checked to determine if they were also affected by the problem. If they were affected, reanalysis of the samples in question is requested from the analytical laboratories. The establishment of the acceptance windows is described in Section 11.

Approximately ninety audit samples are scheduled to be processed during NSS. A statistical evaluation of the audit sample data should provide a good estimate of the bias and precision of the analytical methods for each required measurement. Furthermore, any changes over time in analytical results for the natural-water audit samples without corresponding change in the other audit samples can be attributed to lack of analyte stability.

The findings of a comparative study between audit sample types will provide a statistically valid estimate of the true maximum holding times allowable for each type of analysis.

The audit samples are a key factor in the NSS QA program. It is intended that every effort be made to provide high-quality audit samples.

10.2 Quality Assurance System Audits (On-Site Evaluations)

The systems audit consists of qualitative evaluation of field and analytical laboratory facilities, equipment, and operations such as record keeping, data reporting, and QC procedures.

10.2.1 Field and Mobile Processing Laboratory Operations On-Site Evaluation - Each NSS field base and sampling team can expect at least one on-site evaluation during the course of the sampling effort. This is an on-site inspection to review the sampling procedures, field base operations, sample processing, sample analyses, and QA efforts.

For each field base, the corresponding sampling team, and the mobile processing laboratory, the on-site evaluation should be conducted as soon as possible after the start of monitoring. The questionnaire given in Appendix B is used to assist in the evaluation.

The field auditor conducts an in-depth review of all sampling and processing operations. This includes but is not limited to (a) interviewing the field base coordinator, (b) interviewing each sampling team, (c) accompanying one or more of the sampling teams during a sample excursion, (d) interviewing the supervisor of the mobile processing laboratory, (e) observing operations at the mobile processing laboratory, and (f) writing a summary report that includes results, observations, and recommendations. If any problems are found, the evaluator must either correct them or must bring them to the attention of the field base coordinator or mobile processing laboratory supervisor.

10.2.2 Analytical Laboratory On-Site Evaluation - Each analytical laboratory participating in NSS can expect a minimum of two in-depth, on-site evaluations conducted by the EPA QA manager or the QA manager's authorized representative. The questionnaire in Appendix C is used to assist in the on-site laboratory evaluation.

The first on-site laboratory evaluation is performed after the laboratory has successfully analyzed a set of Pre-Award Performance Evaluation (PE) samples for the contract-required parameters and before the actual survey analytical work begins. The PE samples may contain some or all of the analytes for which determination is required, in the expected concentration ranges. The PE sample results are scored using the NSWS Pre-Award Audit Sample Score Sheet given in Appendix D. Grading emphasizes analytical accuracy, but a substantial portion of the grade depends on meeting the QA, internal QC, reporting, and deliverable requirements.

The auditor summarizes all observations in an on-site laboratory evaluation report and brings all problems that occur to the attention of the laboratory manager for corrective action.

The second on-site laboratory evaluation is conducted after approximately one-third of the NSS analyses have been completed. During the second on-site evaluation, QA sample (audit, duplicate, and blank) data and QC data received to date are reviewed. The laboratory questionnaire is updated, if necessary, to note all changes that have been made since the first on-site evaluation. An on-site laboratory evaluation report is written for this and for each additional on-site laboratory evaluation.

11.0 ACCEPTANCE CRITERIA

11.1 Audit Sample Results

Acceptance windows for single values from audit samples are based on previous interlaboratory analyses of the same sample material. The objective of creating windows is to predict intervals for acceptable single future values based on a sample mean ($\overline{X}$) and sample standard deviation (s) computed from n previously observed values. The limits of the windows are determined by using a t-statistic (t).

$$t = \frac{Z}{\sqrt{\frac{\mu}{r}}} \text{ is a Student's t}$$

where:

Z is the standard normal variate, having a normal distribution with a mean of 0 and a variance of 1

μ is a variable with a chi-square distribution with r degrees of freedom, and Z and μ are independent

The observed values $X_1, X_2, X_3, \ldots X_n$ are independent and have a normal distribution (N) with a population mean (μ) and variance(σ^2). A ($1 - \alpha$) prediction interval or a single future value y is needed. Let X = sample mean and s = sample standard deviation. It is known that:

$$y \sim N\ (\mu, \sigma^2) \text{ and } \overline{X} \sim N \left(\mu, \frac{\sigma 2}{n}\right).$$

Therefore,

$$y - \overline{X} \sim N \left(0, \sigma^2 \ \ 1 + \left(\frac{1}{n}\right)\right).$$

$$Z = \frac{y - \overline{X}}{\sigma\sqrt{1 + \frac{1}{n}}} \sim N(0,\ 1)$$

$$\mu = n-1\left(\frac{s^2}{\sigma^2}\right) \sim x^2_{(n-1)} \quad \text{and}$$

$$r = n-1.$$

Substituting,

$$t = \frac{\dfrac{y - \overline{X}}{\sigma\sqrt{1 + \frac{1}{n}}}}{\sqrt{\dfrac{(n-1)s^2}{(n-1)\sigma^2}}} = \frac{y - \overline{X}}{s\sqrt{1 + \frac{1}{n}}} .$$

The upper and lower limits of the window can be formalized as follows:

$$\overline{X} + (t)(s)\sqrt{1 + \frac{1}{n}} = \text{upper limit of the window}$$

$$\overline{X} - (t)(s)\sqrt{1 + \frac{1}{n}} = \text{lower limit of the window}$$

The Student's t-value (t) has n-1 degrees of freedom. The t-value is for a 2-tailed test with a cumulative probability of 0.95 (i.e., 2.5 percent probability on either side).

For predicting future values, wider windows than the standard 95 percent confidence interval about the mean are desirable. As the number of observed values increases, more variance occurs because of chance alone.

Initially, there may not be sufficient data ($n < 10$) available to provide good interval estimates. Arbitrary criteria may be used until 10 or more values are available. The windows should be periodically updated as more data are accumulated.

Grubbs' test (Grubbs, 1969) is applied to the data before interval estimation to detect outliers. The outliers are excluded from the computation of the windows.

11.2 Duplicate Analysis Results

Acceptance criteria for the RSD are based on the upper 95th percentile of observed values of RSD. Because the RSD is affected by concentration, these criteria are applied only when the mean of the duplicate analyses exceeds the contract-required detection limit (CRDL) by a factor of 10.

Arbitrary acceptance criteria may be used until sufficient (at least 10) RSD values have been observed.

The distribution of the RSD values cannot be estimated accurately until sufficient RSD values have been observed. It is recommended that no outlier test be applied until the distribution has been estimated.

11.3 Blank Analysis Results

Windows for blank analysis results are computationally identical to those for duplicate sample results. Historical data will be used to calculate these windows.

11.4 Corrective Action

Laboratories which fail to meet the acceptance criteria for analysis of audit samples or duplicates are required to repeat the analysis that produced the erroneous results. If results from the second analysis are still unacceptable, further corrective action must be initiated.

12.0 DATA BASE MANAGEMENT SYSTEM

The purpose of the data base management system is to assemble and store data generated as part of NSWS, to provide basic reports of the survey results, to perform statistical analyses describing target populations, and to provide data security. A detailed description of the system is given in the Data Management Proposal (ORNL, 1984; Sale et al., in preparation). The relationship of data base management to the overall NSWS is shown in Figure 12.1.

The data are stored in four major data sets, namely (1) a raw data set, (2) a verified data set, (3) a validated data set, and (4) a final data set. All data sets are protected from unauthorized or accidental access by individual, system, and file password protection.

12.1 Raw Data Set

At ORNL, the Statistical Analysis System (SAG) is used to enter the field and laboratory data (analytical results and data qualifiers - see Table 9.8) reported on Data Forms 4, 5, 11, 13, 18, 19, 20, and 22 into the raw data set. The data package consisting of these forms is also sent to the EMSL-LV QA staff for concurrent data analysis. Data receipt is acknowledged, and field and laboratory personnel verify that all forms are received by the data base management personnel.

The SAS full-screen editor procedure is used to provide initial error checking as data are entered. All data are entered into two separate data sets by two different operators. For the NSWS data base, a custom program (COMPARE) has been developed in SAS to compare the two data sets and to identify any inconsistencies in numeric and alphabetic variables. The advantage of this double entry and comparison process is that typographical errors are identified and are removed from the system.

12.2 Verified Data Set

The raw field and laboratory data are transmitted on magnetic tapes to the EMSL-LV QA group. All data are then evaluated and verified, and appropriate flags (see Table 12.1) are applied to the raw data as described in Section 13.0. The data are processed using the "Automated Quality Assurance Review, Interactive Users System" (AQUARIUS II), an online QA system developed by the EMSL-LV QA staff. Reports generated by AQUARIUS II range in subject from complex protolyte analysis to simple external and internal blank checks for QA purposes (see Table 13.1).

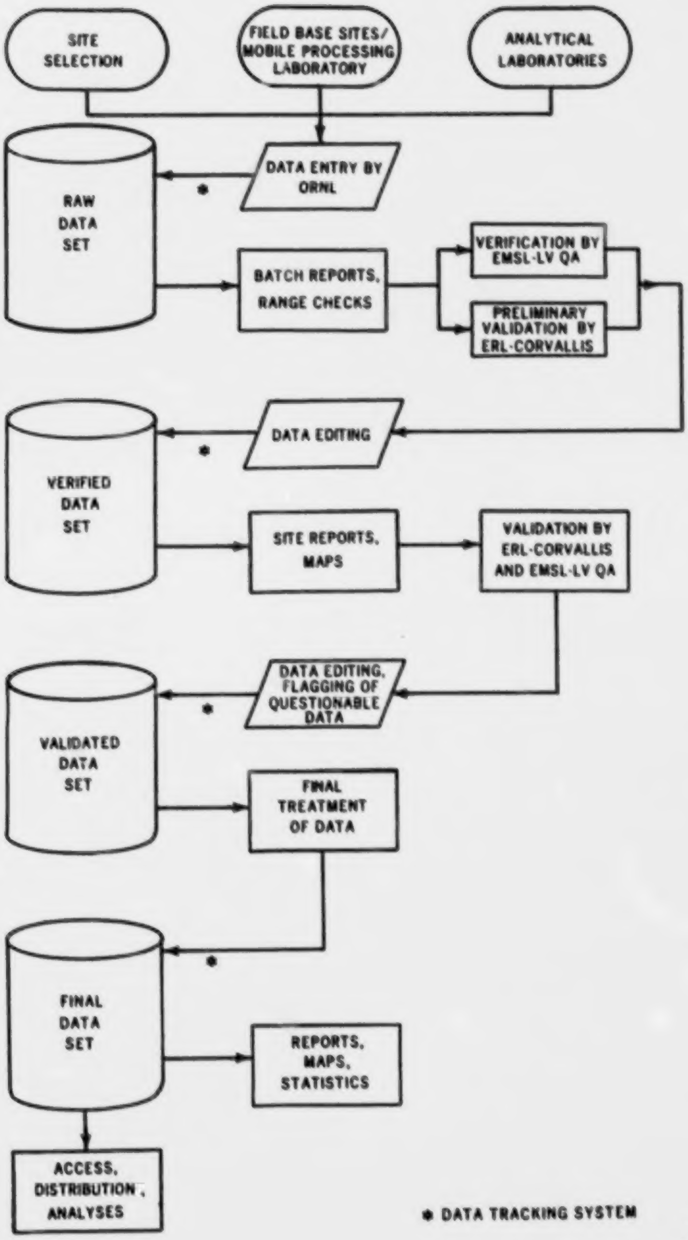

SITE SELECTION
FIELD BASE SITES/ MOBILE PROCESSING LABORATORY
ANALYTICAL LABORATORIES
DATA ENTRY BY ORNL
RAW DATA SET
BATCH REPORTS, RANGE CHECKS
VERIFICATION BY EMSL-LV QA
PRELIMINARY VALIDATION BY ERL-CORVALLIS
DATA EDITING
VERIFIED DATA SET
SITE REPORTS, MAPS
VALIDATION BY ERL-CORVALLIS AND EMSL-LV QA
DATA EDITING, FLAGGING OF QUESTIONABLE DATA
VALIDATED DATA SET
FINAL TREATMENT OF DATA
FINAL DATA SET
REPORTS, MAPS, STATISTICS
ACCESS, DISTRIBUTION, ANALYSES
* DATA TRACKING SYSTEM

Figure 12.1. Data base management for the National Surface Water Survey.

TABLE 12.1. NATIONAL SURFACE WATER SURVEY VERIFICATION DATA QUALIFIERS (FLAGS) FOR RAW DATA SET

FLAGS USED WITH ANION/CATION BALANCE CHECK PROGRAM:

A0	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to unknown cause.
A1	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to unmeasured anions/cations (other anions/cations not considered in %IBD calculation).
A2	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to anion (flag suspect anion) contamination.
A3	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to cation contamination.
A4	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to unmeasured organic protolytes (fits Oliver Model).
A5	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - anion concentration too high (flag suspect anion).
A6	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - cation concentration too low (flag suspect cation).
A7	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - anion concentration too low (flag suspect anion).
A8	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - cation concentration too high (flag suspect cation).
A9	Anion/Cation % Ion Balance Difference (%IBD) is outside criteria due to possible analytical error - alkalinity (ANC) measurement.

FLAGS GENERATED BY APPROPRIATE BLANK EXCEPTION PROGRAM:

B0	External (field) blank is above expected criteria for pH, DIC, DOC, specific conductance, ANC, and BNC determinations.

(continued)

TABLE 12.1. (Continued)

FLAGS GENERATED BY APPROPRIATE BLANK EXCEPTION PROGRAM (continued):

B1	Internal (lab) blank is >2 x CRDL for DIC, DOC, and specific conductance determinations.
B2	External (field) blank is above expected criteria and contributed >20% to sample concentrations. (This flag is not used for pH, DIC, DOC, specific conductance, ANC, and BNC determinations.)
B3	Internal (lab) blank is >2 x CRDL and contributes >10% to the sample concentrations. (This flag is not used for DIC, DOC, and specific conductance determinations.)
B4	Potential negative sample bias based on internal (laboratory) blank data.
B5	Potential negative sample bias based on external (field) blank data.

FLAGS USED WITH CONDUCTANCE BALANCE CHECK PROGRAM:

C0	% Conductance Difference (%CD) is outside criteria due to unknown cause.
C1	% Conductance Difference (%CD) is outside criteria due to possible analytical error - anion concentration too high (flag suspect anion).
C2	% Conductance Difference (%CD) is outside criteria due to anion contamination.
C3	% Conductance Difference (%CD) is outside criteria due to cation contamination.
C4	% Conductance Difference (%CD) is outside criteria due to unmeasured organic ions (fits Oliver Model).
C5	% Conductance Difference (%CD) is outside criteria due to possible analytical error in specific conductance measurement.
C6	% Conductance Difference (%CD) is outside criteria due to possible analytical error - anion concentration too low (flag suspect anion).
C7	% Conductance Difference (%CD) is outside criteria due to unmeasured anions/cations (other anions/cations not considered in %CD calculation).

(continued)

TABLE 12.1. (Continued)

FLAGS USED WITH CONDUCTANCE BALANCE PROGRAM (continued):

C8 % Conductance Difference (%CD) is outside criteria due to possible analytical error - cation concentration too low (flag suspect cation).

C9 % Conductance Difference (%CD) is outside criteria due to possible analytical error - cation concentration too high (flag suspect cation).

FLAGS GENERATED BY DUPLICATE PRECISION EXCEPTION PROGRAM:

D2 External (field) duplicate precision exceeded the maximum expected % Relative Standard Deviation (%RSD), and both the routine and duplicate sample concentrations were ≥10 x Contract Required Detection Limit (CRDL).

D3 Internal (lab) duplicate precision exceeded the maximum contract required % Relative Standard Deviation (%RSD), and both the routine and duplicate sample concentrations were ≥10 x Contract Required Detection Limit (CRDL).

FLAGS USED WHEN FIELD DATA ARE OUTSIDE CRITERIA:

F0 % Conductance difference (%CD) exceeded criteria when in situ field conductance value was substituted.

F1 Hillman/Kramer protolyte analysis program indicated field pH problem when stream site pH value was substituted.

F2 Hillman/Kramer protolyte analysis program indicated unexplained problem with stream site pH or mobile processing laboratory DIC values when stream site pH value was substituted.

F3 Hillman/Kramer protolyte analysis program indicated field problem - mobile processing laboratory pH.

F4 Hillman/Kramer protolyte analysis program indicated field problem - mobile processing laboratory DIC.

F5 Hillman/Kramer protolyte analysis program indicated unexplained problem with mobile processing laboratory pH or DIC values when mobile processing laboratory pH value was substituted.

F6 % Conductance Difference (%CD) exceeded criteria when mobile processing laboratory (trailer) specific conductance value was substituted.

(continued)

TABLE 12.1. (Continued)

FLAGS GENERATED BY HOLDING TIME EXCEPTION PROGRAM:

H0	The maximum holding time criteria were not met.
H1	No "Date Analyzed" data were submitted for reanalysis data.

FLAG GENERATED BY DETECTION LIMIT EXCEPTION PROGRAM:

L1	Instrumental Detection Limit (IDL) exceeded Contract Required Detection Limit (CRDL) and sample concentration was <10 x IDL.

MISCELLANEOUS FLAG:

M0	Value obtained using a method which is unacceptable as specified in the Invitation for Bid (IFB) contract.

FLAGS GENERATED BY AUDIT CHECK PROGRAM:

N0	Audit sample value exceeded upper control limit.
N1	Audit sample value was below control limit.

FLAGS GENERATED BY HILLMAN/KRAMER PROTOLYTE ANALYSIS PROGRAM:

P0	Lab problem - initial pH from alkalinity (ANC) titration.
P1	Lab problem - initial pH from acidity (BNC) titration.
P2	Lab problem - unexplained - initial pH from ANC or BNC titration.
P3	Lab problem - initial DIC determination.
P4	Lab problem - air-equilibrated pH or DIC determinations.
P5	Lab problem - unexplained - initial pH from ANC or BNC titrations or initial DIC determinations.
P6	Lab problem - alkalinity (ANC) determination.

(continued)

TABLE 12.1. (Continued)

FLAGS GENERATED BY HILLMAN/KRAMER PROTOLYTE ANALYSIS PROGRAM (continued):

P7 Lab problem - CO_2-Acidity (BNC) determination.

FLAGS GENERATED BY QCCS EXCEPTION PROGRAM(S):

Q1 Quality Control Check Sample (QCCS) was above contractual criteria.

Q2 Quality Control Check Sample (QCCS) was below contractual criteria.

Q3 Insufficient number of QCCS were measured.

Q4 No Quality Control Check Sample (QCCS) was analyzed.

Q5 Detection Limit QCCS was not 2 to 3 X Contract Required Detection Limit (CRDL) and measured value was not within 20% of the theoretical concentration.

MISCELLANEOUS FLAGS:

X0 Invalid but confirmed data based on QA review.

X1 Extractable Al concentration is greater than total Al concentration by 0.010 mg/L where extractable Al $\geq$ 0.015 mg/L.

X2 Invalid but confirmed data - potential aliquot switch.

X3 Invalid but confirmed data - potential gross contamination of aliquot or parameter.

X4 Invalid but confirmed data - potential sample (all aliquots) switch.

Values for flags X0 through X4 should not be included in any statistical analysis.

MISSING VALUE CODE

"." Value never reported.

(Note: This code appears in numeric fields only.)

For the Pilot Survey, as for the Eastern Lake Survey - Phase I, AQUARIUS was used to generate exception tuples (change records) that were sent to ORNL for implementation. For the other three NSS surveys, a modified system called the Aquatics Analysis System (AQUARIUS II) was developed based on transaction processing. Rather than generating and applying tuples, the modified system generates data changes in the form of transaction records from exception programs and from manually edited records copied from a local master data base (LMD). These transaction records can be used by the EMSL-LV QA group and by ORNL to update the LMD and the official raw data set, respectively. Results of EMSL-LV QA group verification consist of a copy of the updated LMD and a history file that contains the transaction records that were used to update the LMD. A detailed flow scheme of the Aquatics Analysis System is presented in Figure 12.2.

In addition to the standard QA analyses, AQUARIUS II is used to generate various printouts supplied to the QA manager to point out intralab, interlab, and interfield bias, as well as discrepancies in blanks, audits, or other QA samples. The overall outcome is a verified data set in which all questionable values are qualified. The QA personnel coordinate with the field bases, the mobile processing laboratory, and the analytical laboratories to make all appropriate corrections in the data.

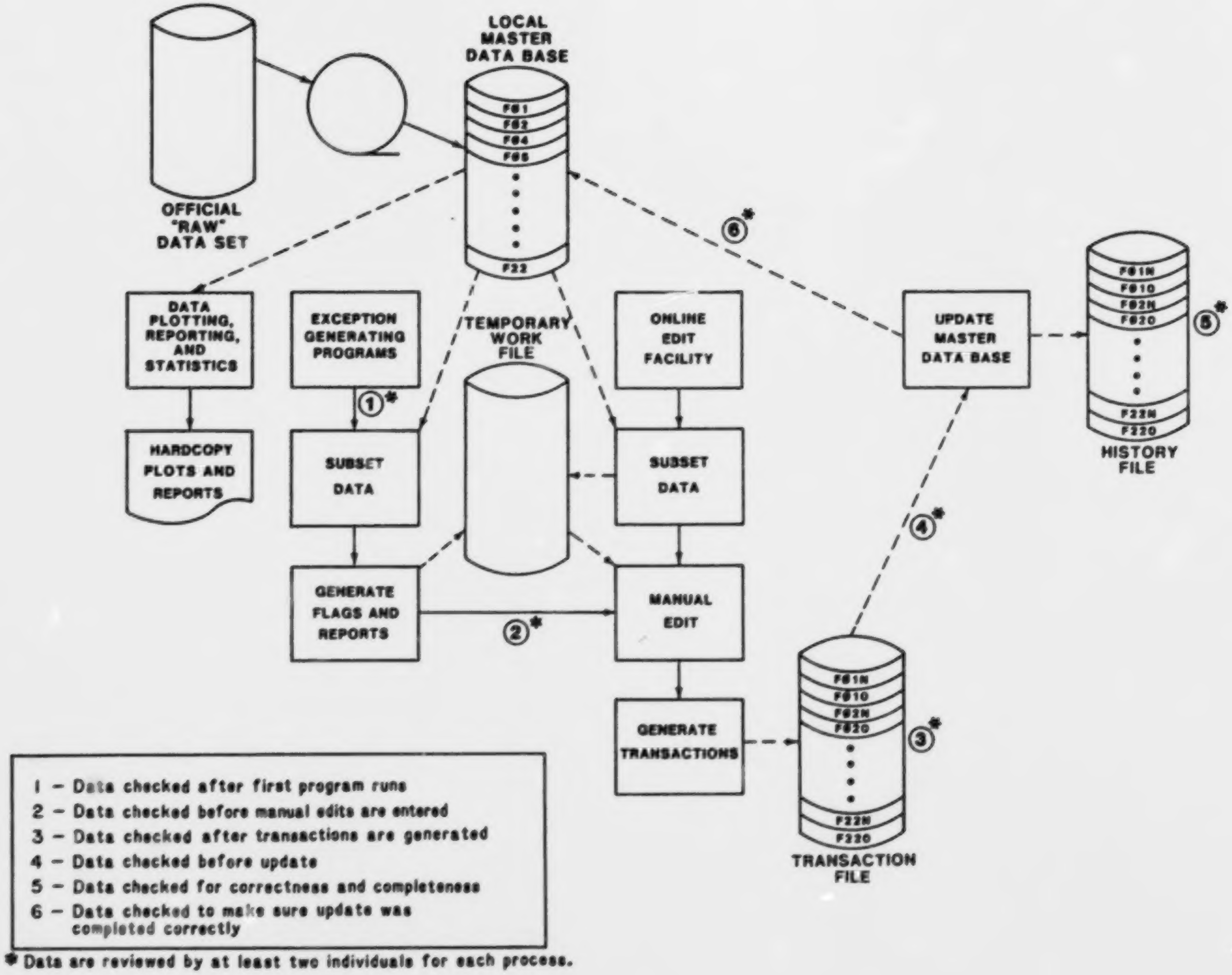
12.3 Validated Data Set

The verified data set is provided to the ERL-C staff on a magnetic tape, and the staff initiates the validation process. The validation process increases the overall integrity of the data base by evaluating all data for internal and regional consistency using all QA and QC information available.

The validation process compares data for a set of variables against a more restricted range utilizing knowledge of relationships in aquatic chemistry and limnology to identify intersite sample inconsistencies. Intersite validation consists of comparing single site values with values from adjacent sites within a region. Data for groups of sites are compared to check for consistency. The validation process is discussed further in Section 14.0. After undergoing this review process, the data, site by site, are transferred to the validated data set.

12.4 Final Data Set

Calculating population estimates is difficult if values are missing from the data set. A final data set (Data Set 4) is prepared to resolve such problems by inserting reliable values where ones are missing in the validated data set (Data Set 3). Data Set 4 also is modified from Data Set 3 by averaging field duplicate values (if QA precision criteria are met)


OFFICIAL "RAW" DATA SET
LOCAL MASTER DATA BASE
F01
F02
F04
F05
F22
DATA PLOTTING, REPORTING, AND STATISTICS
HARDCOPY PLOTS AND REPORTS
EXCEPTION GENERATING PROGRAMS
①*
SUBSET DATA
GENERATE FLAGS AND REPORTS
TEMPORARY WORK FILE
②*
ONLINE EDIT FACILITY
SUBSET DATA
MANUAL EDIT
GENERATE TRANSACTIONS
F01N
F010
F02N
F020
F22N
F220
TRANSACTION FILE
③*
④*
UPDATE MASTER DATA BASE
⑥*
F01N
F010
F02N
F020
F22N
F220
HISTORY FILE
⑤*

1 – Data checked after first program runs
2 – Data checked before manual edits are entered
3 – Data checked after transactions are generated
4 – Data checked before update
5 – Data checked for correctness and completeness
6 – Data checked to make sure update was completed correctly

* Data are reviewed by at least two individuals for each process.

Figure 12.2 Aquatics Analysis System (AQUARIUS II).

and by replacing analytical values determined during validation to be erroneous.

In those cases where a value is missing or incorrect (i.e., the value is identified as an outlier during validation and the aberration is not a result of an episode or some site condition) and a new value must be incorporated, the new value is obtained from one of the following sources, listed from most to least desirable:

1. Value from the duplicate of an R/D pair for the routine value.

2. Value from an alternate sample.

3. Value of a redundant measurement on the same sample.

4. Value predicted from the best regression of related variables (e.g., Ca vs. ANC, pH vs. ANC) or from the best regression of the same variables; these regressions include all comparisons and combinations.

If there are four or more variables identified as outliers for the same sample, the site is considered unusual.

Another modification is that negative values for parameters other than ANC that resulted from analytical calibration bias are set equal to zero. The bias in the estimate of variance due to this adjustment is not expected to affect data analyses. All values modified in the final data set are flagged. After the final data set is completed, the data will be released by EPA and will be made available to all data users.

13.0 DATA EVALUATION AND VERIFICATION

As the field and analytical laboratory data are received by the EMSL-LV QA staff, all data are evaluated based on the available QA and QC information, using the established and organized review process described here. The objective of the data verification process is to identify, correct, or flag data of unacceptable quality. Computer programs have been developed to automate this process as much as possible. Each batch of data is evaluated on a sample-by-sample basis, as described in the following sections. Figure 13.1 is a summary of the verification process.

13.1 Field Data Review

Each field data form is reviewed to check for the following items:

1. Stream ID. Forms 4, 4A, 6, and 7 are compared to Form 5 to identify and correct transcription errors.
2. Trailer Duplicate. On Form 5, a duplicate stream sample ID should match a routine stream sample ID.
3. pH. The streamside pH reading recorded on Form 4 is compared to the mobile processing laboratory pH reading on Form 5. The difference must be $\leq$ 0.3 pH units.
4. Mobile Processing Laboratory pH, DIC, Specific Conductance, and Nonexchangeable and Total PCV Reactive Aluminum. Form 5 measurements for field audit samples are evaluated in accordance with the associated acceptance criteria. Routine-duplicate pairs and trailer duplicate pairs are also evaluated for precision.
5. DIC, pH, Specific Conductance, and Nonexchangeable and Total PCV Reactive Aluminum QCCS Data. Form 5 QCCS data are evaluated to ensure that QCCS criteria are met.
6. Data Qualifiers. Comments and data qualifiers are reviewed for correct use and consistency.

Data anomalies are reported to the mobile processing laboratory coordinator for review, and data reporting errors are reported to ORNL to be corrected before entry into the raw data set. All telephone communications are recorded in bound notebooks, and data corrections (e.g., transcription errors, missing data, incorrect units, and incorrect use of data qualifers) are annotated on the appropriate forms before they are sent to ORNL for data entry.

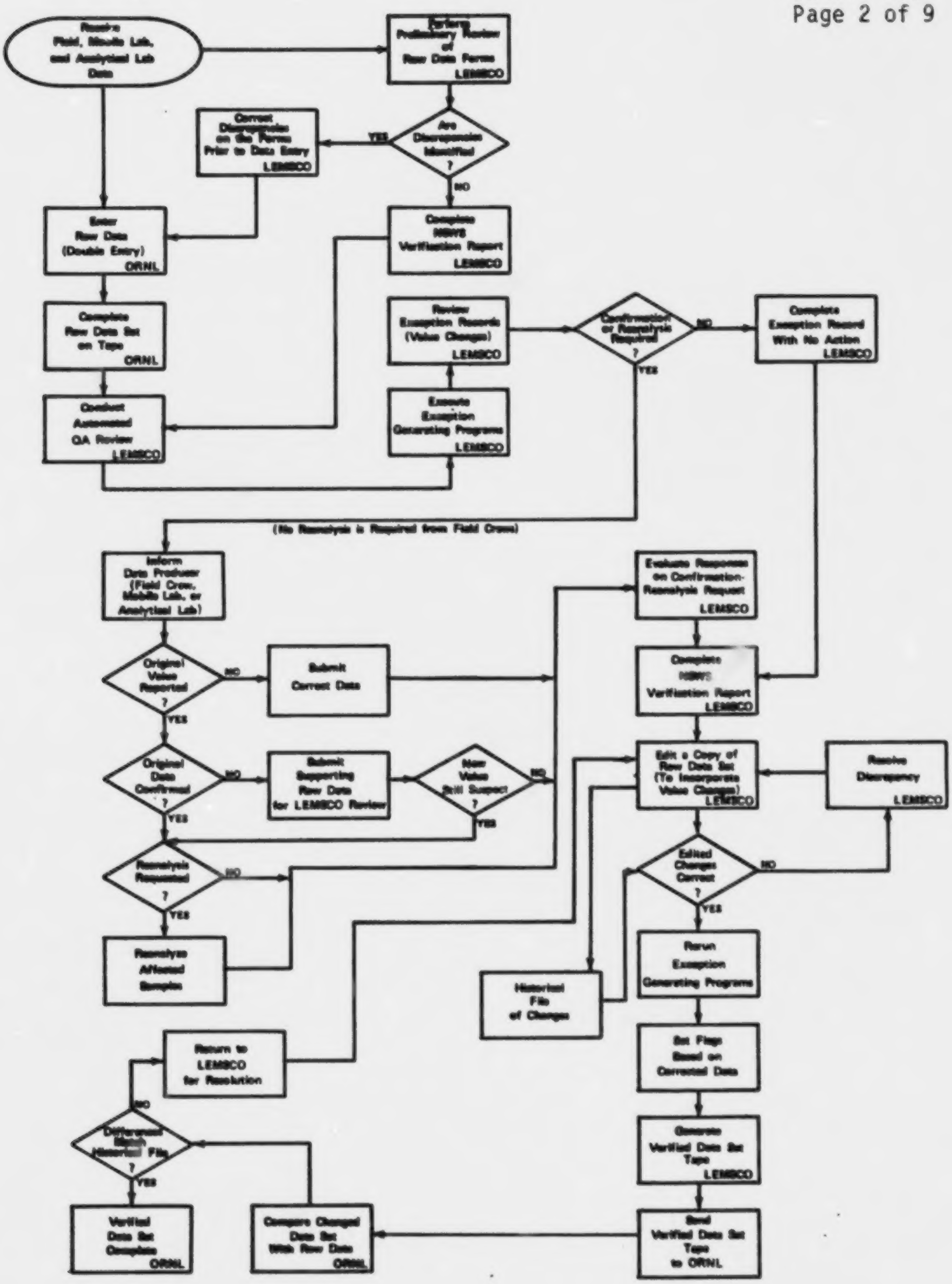

Receive Field, Mobile Lab, and Analytical Lab Data
Perform Preliminary Review of Raw Data Forms LEMSCO
Are Discrepancies Identified ?
YES
NO
Correct Discrepancies on the Forms Prior to Data Entry LEMSCO
Enter Raw Data (Double Entry) ORNL
Complete NSWS Verification Report LEMSCO
Complete Raw Data Set on Tape ORNL
Conduct Automated QA Review LEMSCO
Execute Exception Generating Programs LEMSCO
Review Exception Records (Value Changes) LEMSCO
Confirmation or Reanalysis Required ?
NO
YES
Complete Exception Record With No Action LEMSCO
(No Reanalysis is Required from Field Crews)
Inform Data Producer (Field Crew, Mobile Lab, or Analytical Lab)
Original Value Reported ?
NO
YES
Submit Correct Data
Evaluate Responses on Confirmation-Reanalysis Request LEMSCO
Complete NSWS Verification Report LEMSCO
Original Data Confirmed ?
NO
YES
Submit Supporting Raw Data for LEMSCO Review
New Value Still Suspect ?
NO
YES
Edit a Copy of Raw Data Set (To Incorporate Value Changes) LEMSCO
Resolve Discrepancy LEMSCO
Reanalysis Requested ?
NO
YES
Edited Changes Correct ?
NO
YES
Reanalyze Affected Samples
Historical File of Changes
Rerun Exception Generating Programs
Return to LEMSCO for Resolution
Set Flags Based on Corrected Data
Differences Match Historical File ?
NO
YES
Generate Verified Data Set Tape LEMSCO
Verified Data Set Complete ORNL
Compare Changed Data Set With Raw Data ORNL
Send Verified Data Set Tape to ORNL

Figure 13.1. Flowchart for data verification process.

13.2 Analytical Data Review

13.2.1 Daily Quality Assurance Communications - Daily calls are made to each field base, to the mobile processing laboratory, and to each analytical laboratory to ensure that QA and QC guidelines are being followed and that samples are being handled and analyzed properly, to obtain current sample data, and to discuss problems that may occur during analyses.

The primary objective of these calls is to identify and resolve issues quickly, before they affect data quality or interfere with the completion of the survey. Preliminary sample data are obtained verbally or by computer, depending on the capabilities of the analytical laboratory. The preliminary data are evaluated by comparing the QA sample data against acceptance criteria. Responsible parties are notified of problems and all interactions are recorded in bound notebooks.

13.2.2 Preliminary Review of Sample Data Package - The sample data packages are reviewed for completeness, internal QC compliance, and appropriate use of data qualifiers. The Data Package Completeness Checklist in the verification report (given in Appendix E) is used to assure consistency in the review of all data packages. Any discrepancies related to analytical data are reported to the appropriate analytical laboratory manager for corrective action. If discrepancies affect billing or data entry, then SMO or ORNL is notified. Comments provided in the cover letter are also reviewed to determine their impact on data quality and the need for any follow-up action by the laboratory. This data review process is also important in verifying that the contractual requirements are met for the purpose of payment.

13.2.3 Review of Quality Assurance and Quality Control Data - The analytical data reported on data forms are entered into the raw data set by ORNL as the data packages are received. A magnetic tape containing raw data is sent to the National Computer Center (NCC), Research Triangle Park, North Carolina, for use on the EPA IBM 3081 computer. Each tape received by the NCC tape library is given a volume serial number and a BIN number that indicates the physical location of the tape. The tape is loaded remotely by the EMSL-LV QA staff, and exception programs, listed in Table 13.1, are generated by AQUARIUS II.

The NSS Verification Report (Appendix E) is completed with the use of outputs from exception reports (along with the original data, mobile processing laboratory data, and field notebooks). The verification report is a worksheet designed to systematically guide the auditor through the verification process by explaining how to flag data, tracking data resubmissions, tracking reanalysis and confirmation requests, listing the steps to help explain the QA exceptions, summarizing all modifications to the raw data set, and listing all flagged sample data.

TABLE 13.1. EXCEPTION GENERATING AND DATA REVIEW PROGRAMS OF AQUARIUS II

Program	Type
Exception Generating Programs:	
1 = Audit Sample Summary	(FL,LL,FN,LN)
2 = Field Blank Summary	(B)
3 = Field Duplicate Precision Summary	(R/D Pairs)
4 = Instrumental Detection Limit Summary	(All Species)
5 = Holding Time Summary	(All Species)
6 = % Conductance Difference Calculations	(All Species)
7 = Anion/Cation Balance Calculations	(All Species)
8 = Internal Lab Duplicates	
9 = Protolyte Analysis (DIC, pH, ANC, and BNC Data Evaluation)	
10 = Reagent/Calibration Blanks, QCCS, and Detection Limit QCCS	
Data Review Programs:	
1 = Raw Data Listing - Format for QA Manager	
2 = Complete Raw Data Listing - Format for Audit Staff	
3 = Comparison of Form 4 and Form 5	(pH and DIC)
4 = Comparison of Form 5 and Form 11	(pH and DIC)
5 = QA/QC Flag Summary	
6 = Modified Gran Analysis Program	

One hundred percent of the analytical data are verified, sample by sample. Stream sample analytical data that meet the anion/cation %IBD, the %CD, and the internal and external QA and QC criteria can be regarded with a high degree of confidence. If the %IBD or %CD results are outside the specified limits but the discrepancy can be explained by either the presence of organic species (as indicated by the protolyte analysis program) or an obvious correctable reporting error, the data are still verified by the EMSL-LV QA staff.

Additional flags are applied to a given parameter, even though the verification is on a "per sample" basis, when the batch QA sample data do not meet the acceptance criteria for QA samples such as field blanks, field duplicates, or audit samples. Each parameter is also flagged if internal QC checks such as calibration and reagent blank analytical results, internal duplicate precision, instrumental detection limits, QCCS analytical results, and required holding times do not meet specifications. The final source of flags is the protolyte analysis program. A detailed description of the evaluation of DIC, pH, ANC, and BNC data by the protolyte analysis program is given in Section 13.2.4. In all cases, the flags that are generated by the computer programs are reviewed by the auditor for reasonableness and consistency before they are entered into the verified data set.

13.2.4 Computer Evaluation of DIC, pH, ANC, and BNC Data by Protolyte Analysis - An evaluative computer program performs data checks and uses carbonate equilibria and DOC data to identify analytical error and the source of protolytes (acidic or basic species) in the sample. Thus, the DIC, pH, ANC, and BNC data are rigorously evaluated in light of known characteristics of carbonate equilibria. The overall process of data evaluation based on carbonate equilibria is summarized below.

13.2.4.1 Redundant Alkalinity Checks for pH and DIC - Evaluations of carbonate equilibria indicate that alkalinity is not affected by changes in dissolved CO_2 concentration. Furthermore, alkalinity can be calculated from carbonate equilibria if the DIC and pH are known. A theoretical alkalinity, C, is calculated from each of the three pH/DIC pairs:

C_1 = pH/DIC of "closed system" syringe samples (mobile processing laboratory)

C_2 = pH/DIC of "open system" samples (analytical laboratory)

C_3 = pH/DIC of "air-equilibrated system" samples (analytical laboratory)

The third data pair is obtained on an aliquot that has been equilibrated with standard air (300 ppm CO_2). If there is no analytical error, the three calculated alkalinities should agree within the limits of experimental error. The precision for calculated alkalinity values of less than or equal to 100 μeq/L should be within 10 μeq/L and within 10 percent for calculated alkalinity values greater than 100 μeq/L. The precision windows are based on the estimated precision of the pH and DIC measurements used in the calculations. If this comparison indicates a potential analytical error (i.e., the precision limit is exceeded), the redundant pH and DIC values are compared to identify the source of error. Further evaluation of the QA and QC information for the individual data pairs usually identifies one of the pH or DIC measurements within the outlier pair as the source of error. Because the measurement is redundant, an acceptable pH or DIC value from one of the data pairs should be available to the data user for every sample that is analyzed.

13.2.4.2 Verification of Measured ANC - The measured ANC is evaluated by comparing it to the average of the acceptable calculated values for alkalinity determined during the evaluation of pH and DIC.

Carbonate Systems - For a true carbonate system, the measured ANC should equal (within the limits of experimental error) the calculated alkalinity. The difference between measured ANC and the calculated alkalinity should be within 15 μeq/L for calculated alkalinities less than or equal to 100 μeq/L, and within 10 percent for larger values. If the measured ANC differs from the calculated alkalinity, an analytical error is indicated in the titration or in the pH or DIC measurements.

Mixed Systems - Mixed systems are those represented by samples that have significant concentrations of other protolytes in addition to the carbonate species. In natural waters, weak conjugate bases of natural humic and fulvic acids are often present and can contribute significantly to the ANC. The acidic functional groups of natural humic substances contribute to the BNC of natural waters as well. Two empirical relationships among DOC, pH, and organic protolytes have been proposed by Oliver et al. (1983). The first relates the total organic protolyte to DOC, and the second relates the mass action quotient (pKo) of the organics present to the sample pH.

DOC and pH are measured in each sample. The empirical relationships (defined by the Oliver model) and the measured pH and DOC values are used to estimate the contribution of organic protolytes to the measured ANC. The measured ANC should equal, within experimental error, the sum of the calculated alkalinity and the estimated organic protolyte contribution, assuming that significant concentrations of other non-organic protolytes are not present and there is no analytical error. The precision should be within 15 μeq/L for calculated ANC less than or equal to 100 µeq/L and within 10 percent for larger values.

13.2.4.3 Verification of Measured BNC - BNC, unlike ANC, is affected by changes in dissolved CO_2 concentration. Therefore, evaluation and verification of those data cannot utilize as much redundancy as that of ANC data. Only the initial pH and DIC values determined in the analytical laboratory (data pair C_2) can be used to calculate BNC for comparison with the measured value. As with ANC, other protolytes can contribute to the measured BNC. An estimate of CO_2-acidity is calculated from data pairs and carbonate equilibria. If no other protolytes are present, the calculated acidity should equal, within the limits of experimental error, the measured BNC. Precision for calculated acidity values less than or equal to 100 µeq/L should be within 10 µeq/L and within 10 percent for larger values. If the calculated acidity is greater than the measured BNC, an analytical error in the pH, DIC, or BNC determination is indicated.

The pH and DIC measurements are verified by the previous tests (QA/QC redundancy and alkalinity checks). If the calculated acidity is less than the measured BNC, the difference may be due to the presence of other protolytes or to an analytical measurement error. The Oliver model is used to evaluate the contribution from organic acids.

13.2.4.4 System Check for Total Carbonate - For a carbonate system, it can be shown that the sum of alkalinity and acidity equals total carbonate concentration in the sample. For a mixed system, it can be shown that the sum of ANC and BNC equals the total protolyte concentration in the sample. Thus, the calculated values of alkalinity and acidity can be combined and compared to the sum of the measured ANC and BNC, as an additional check of the data. For a carbonate system, the sum of ANC and BNC should equal, within the limits of experimental error, the total carbonate concentration or the sum of calculated acidity and alkalinity. If this sum is less than the calculated total carbonate, an analytical error is indicated because the two titrations must account for all carbonate species present in the sample. Other protolytes or analytical error is indicated if the sum of ANC and BNC exceeds the calculated total carbonate. Again, the Oliver model is used to evaluate the data.

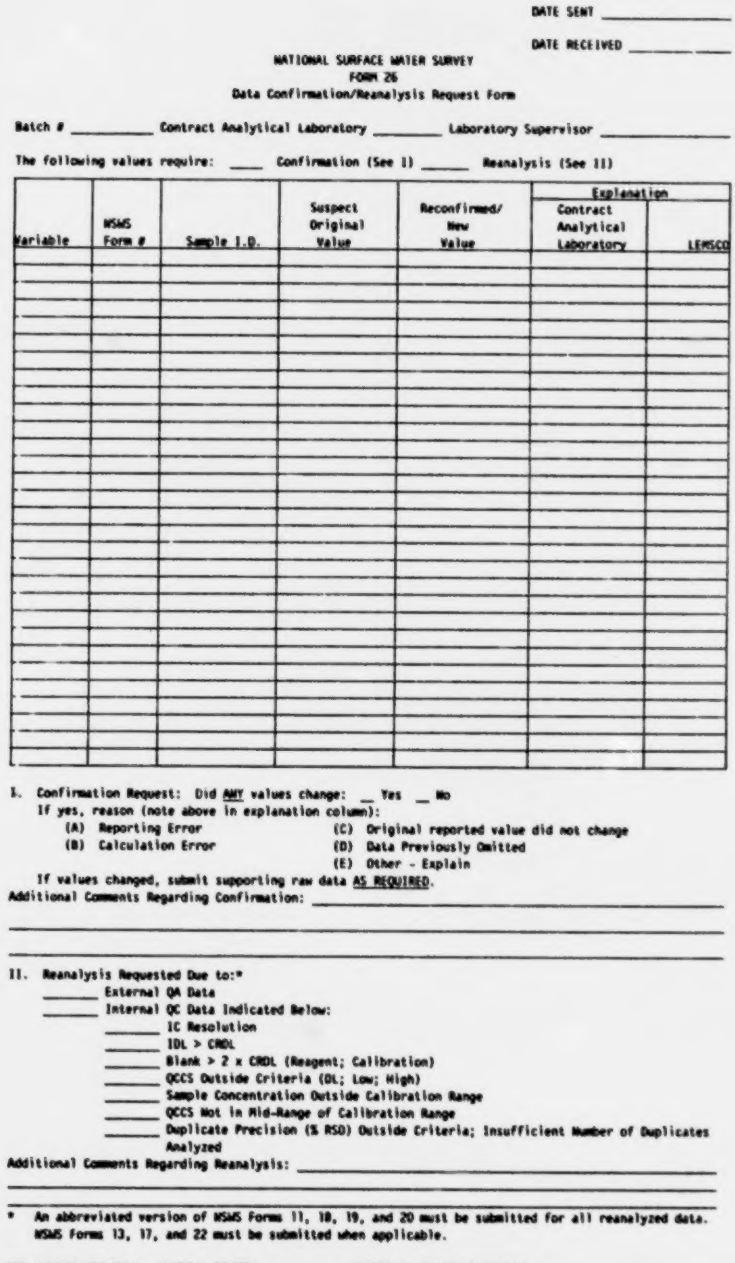
The precision for this evaluation should be within 15 µmole/L for total carbonate concentrations less than or equal to 100 µmole/L, and within 10 percent for higher concentrations.

The protolyte analysis program generates flags (Table 12.1), based on the data checks described above, to indicate the source of problems. Flowcharts that demonstrate these data checks are available from EMSL-LV.

13.2.5 Follow-up with Analytical Laboratories - After the review of all data is completed, the analytical laboratories are requested to resubmit data reporting forms that are incomplete, to submit corrections of previously reported data, to confirm previous results, and to reanalyze certain samples that do not meet QA and QC criteria. In certain cases, the EMSL-LV QA staff may request that the analytical laboratory submit the raw data for a particular sample or batch. These raw data are used (1) to evaluate data anomalies not easily explained or corrected during the data review process and (2) to support requests for sample reanalysis or value confirmation. The analytical laboratories are required to submit confirmation and reanalysis data on Form 26 (see Figure 13.2). The analytical laboratories are directed to respond within a reasonable time so that the results are evaluated in time for them to be useful to the survey.

13.2.6 Evaluation of Outliers Generated by Corvallis Staff - During the verification process, outliers (defined in Section 14.2) identified by the ERL-C staff are examined further by the EMSL-LV QA staff. For any of these outliers not identified previously, confirmation of the value is requested from the contract analytical laboratory. Any value changes are incorporated into the changed data set before it is sent to ORNL.

13.2.7 Preparation and Delivery of Verification Tapes - The steps identified in Sections 13.2.2 through 13.2.6 are followed to identify suspect data and to correct erroneous data. The information obtained by this process is accumulated by the EMSL-LV QA staff and is placed on magnetic tapes, which are sent to ORNL. There, the new data and qualifiers are entered into the raw data set to correct and flag the original data. The identification and transfer of corrected data for entry into the verified data set are described more fully in Section 12.



DATE SENT ______________

DATE RECEIVED ______________

NATIONAL SURFACE WATER SURVEY
FORM 26
Data Confirmation/Reanalysis Request Form

Batch # __________ Contract Analytical Laboratory ________ Laboratory Supervisor ______________

The following values require: ____ Confirmation (See I) ______ Reanalysis (See II)

Variable	NSWS Form #	Sample I.D.	Suspect Original Value	Reconfirmed/ New Value	Explanation	
					Contract Analytical Laboratory	LEMSCO

I. Confirmation Request: Did ANY values change: __ Yes __ No
If yes, reason (note above in explanation column):
(A) Reporting Error
(B) Calculation Error
(C) Original reported value did not change
(D) Data Previously Omitted
(E) Other - Explain
If values changed, submit supporting raw data AS REQUIRED.
Additional Comments Regarding Confirmation: ______________________________

II. Reanalysis Requested Due to:*
_______ External QA Data
_______ Internal QC Data Indicated Below:
  _______ IC Resolution
  _______ IDL > CRDL
  _______ Blank > 2 x CRDL (Reagent; Calibration)
  _______ QCCS Outside Criteria (DL; Low; High)
  _______ Sample Concentration Outside Calibration Range
  _______ QCCS Not in Mid-Range of Calibration Range
  _______ Duplicate Precision (% RSD) Outside Criteria; Insufficient Number of Duplicates Analyzed
Additional Comments Regarding Reanalysis: ______________________________

* An abbreviated version of NSWS Forms 11, 18, 19, and 20 must be submitted for all reanalyzed data. NSWS Forms 13, 17, and 22 must be submitted when applicable.

FOR LEMSCO USE ONLY: INITIAL REVIEW __________ NUMBER OF VALUES SUBMITTED ______________
VERIFICATION __________ NUMBER OF VALUES CHANGED ______________

Figure 13.2. National Surface Water Survey Form 26 - Data Confirmation/Reanalysis Request.

14.0 DATA VALIDATION

14.1 Overview

Validation, in the context of data bases, is the process by which data are evaluated for quality consistent with the intended use of the information. Because validation is a process linked to the goals and methods of a project, the process must be defined for each data base. Consequently, no single set of criteria can be applied to all data bases to judge their validity. Validation is, therefore, a functional term for describing the continuing process of defining the quality of the data with each step resulting in increased knowledge of, and presumably confidence in, the data. This is accomplished by reviewing the data for errors; data known to be erroneous are identified so that correct data can be substituted, and possible errors are flagged to alert the user to their questionable status.

In the verification step, which precedes validation, the quality of the analytical chemical data is determined through a rigorous protocol based on known principles of chemistry. However, not all potential errors in the data are evaluated in the verification process. Verification scrutinizes the internal consistency of chemical concentrations within a sample; the validation process seeks to determine the plausibility of sample physical and chemical data in the context of a subregional set of samples. Therefore, the purpose of the validation process for NSWS is to investigate errors in the chemical analyses not detected in verification and to provide a review of the quality of the nonchemical variables. The list of some physical variables subject to validation is shown in Table 14.1.

Two aspects of the data validation process are the identification of outliers and the evaluation of possible systematic error in the measurement process. Both of these aspects are exploratory, as opposed to test-oriented, and as such, the methods stress visual presentations and subjective, though conservative, selection procedures. The objective is to attract attention to certain data values or sets of values so that special thought and caution will be applied to them during data analysis and model building. The methods selected for detection of outliers and systematic errors were chosen for their simplicity of implementation from a computational standpoint and for the degree of their ability to use pre-existing software.

The techniques to be used in validating the Mid-Atlantic Phase I data are essentially the same as those used for the Phase I - Pilot Survey. The major difference lies in the type of special univariate techniques to be employed. In the Phase I - Pilot Survey, univariate fences were used to evaluate individual streams; this was possible because large numbers of observations were available for each site. In the Mid-Atlantic Phase I study, there is a maximum of four routine samples per site, and this

TABLE 14.1. SOME PHYSICAL VARIABLES SUBJECT TO VALIDATION

Variable	General Description of Validation Checks
1. Latitude 2. Longitude 3. Elevation 4. Watershed Area	Stream location is compared to location measured on USGS maps.
5. Stream Inlets and Outlets	Stream characteristics are checked against state records, where available, to confirm stream identification.
6. Streambank Land Use	Data are compared to aerial photographs.
7. Water Temperature	Recorded temperature is checked to see if it falls in appropriate range.
8. True Color 9. Turbidity	Data are checked for internal consistency.

precludes use of the fence technique. In place of the fences, univariate ratio comparisons are made. These ratios are computed as follows:

1. $$\frac{\text{Downstream-Upstream Observation}}{\text{Upstream Observation}}$$

2. $$\frac{\text{Downstream1-Downstream2 Observation}}{\text{Downstream1 Observation}}$$

3. $$\frac{\text{Upstream1-Upstream2 Observation}}{\text{Upstream1 Observation}}$$

For Southeast Screening Survey sites, only ratio 1 is computed.

Following ratio computations, each ratio is subjected to univariate analysis to determine underlying distributions. Paired t-tests are made to discern if there is a significant difference between the test subpopulations. If there is a significant difference, the actual ratio values are inspected for high (and low) extremes, which represent outliers. This technique identifies outlier pairs in actuality, specific to the ratio formula employed. In practice, only those values above 2X the system detection limit or 1/2 the quantitation limit are passed into these analyses.

The data are divided into 10 subsets that correspond to the discrete Mid-Atlantic and Southeast Screening subregions (or parts thereof). Each subset is evaluated individually via principal component analysis (PCA). (Missing values at this level are substituted by subset means.) Multivariate suites are extracted from the scoping PCA where at least 95 percent of the model variance is displayed; i.e., the number of principal components that demonstrate 95 percent of the cumulative variance of the model is the cutoff number for multivariate suites. The PCA cross-correlation matrix is used to define one bi- or multiple-linear regression model for each variable. Therefore, there are 38 suites for regression analyses plus n suites for restricted PCA and cluster analyses (in 2D, 14 PCA/CLUS suites were defined).

14.2 Detection of Outliers

Outliers are defined as observations that are not typical of the population from which the sample is drawn. They are identified using univariate, bivariate, and multivariate analyses. These procedures assist in identifying outliers that require further scrutiny. However, observations that are atypical with respect to the population may result from analytical error or heterogeneity in chemistry among streams. It is essential to separate analytical errors from abnormal stream chemistry to avoid the undesirable effect of purging analytically correct values from the data base (discussed in Section 14.4).

14.2.1 Frequency Analyses - A SAS procedure is used to produce a 1-, 2-, 3-, 4-, and 5-way frequency and crosstabulation (PROC FREQ) in order to determine completeness of the data set. Outputs may be organized:

- by stream ID to determine duplicate entries, entry errors, and missing values
- by batch ID, sample ID, and sample code to determine duplicate entries, invalid entries, and missing values
- by variable (e.g., mobile laboratory pH measurement) to determine invalid entries and missing values.

14.2.2 Univariate Analyses - An initial approach to outlier detection is to consider each variable individually and to search for values that are extreme with respect to the sample. The method used here is the box plot (Tukey, 1977) as implemented in SAS (SAS Institute, 1982). The box plot summarizes the data for one variable based on the median and upper (Fu) and lower (Fl) fourths or quartiles. The difference between the upper and lower quartiles is known as the inter-quartile range (Fu - Fl = dF); any value greater than the absolute value of 3 dF is identified as an outlier.

Summary statistics with plots are used to identify five high and low extreme values to determine underlying distributions, to flag extreme values, and to assess data variability. These statistics are performed on the entire data base, the spring data set, the spring upper and lower node measurements, the summer data measurements, the summer upper and lower node measurements, and individual streams.

Univariate windows for each variable determine "unusual" values for a given stream. This method involves using by-stream quartiles computed by SAS under Definition No. 1 (SAS, 1985, p. 1186):

weighted average of x_{np}

$$y = (1 - g)\, x_j + g\, x_j + 1$$

where:

$np = j + g$

and x_0 is taken as x_1

x = a value for the variable

y = the tth percentile where j is the integer part and g is the fractional part of np.

The difference between the values for the first and third quartiles is used to compute inner and outer, upper and lower windows for each stream and variable as follows:

```
                     --------Q DIFF----------
                     |                      |
                     Q1                     Q3
||---------|---------|--------Median----------|-------------|--------||
outer      inner     25th                    75th          inner    outer
    lower         percentile              percentile          upper
    window     (first quartile)        (third quartile)       window
```

where:

inner lower = Q1 - (1.5 x Q DIFF)
outer lower = Q1 - (3.0 x Q DIFF)

inner upper = Q3 + (1.5 x Q DIFF)
outer upper = Q3 + (3.0 x Q DIFF)

Following window computations, all data are compared to their appropriate windows. One data set is prepared that contains the by-stream window statistics. Other data sets are also prepared, one for each inner and outer, lower and upper window so that values that fall outside the inner, inner and outer, lower and upper windows are identified. These data are then screened to determine whether they are "outliers" (from the traditional definition) or episodes, polluted, etc. Outliers are reported to the EMSL-LV QA staff for further verification.

14.2.3 Principal Components Analysis - The objective of this analysis is to determine multivariate associations to be used in establishing bivariate, multiple linear regression, and sets of multivariate statistical tests for advanced statistical analysis. Relationships among variables are presented in Table 14.2.

14.2.4 Bivariate Analyses - Although values of two variables may not be outliers within their respective univariate distributions, the pair may be consiered extreme relative to some expected or typical relationship. Scatter plots are useful for examining expected theoretical or empirical relationships between variables. The bivariate relationships examined in this process are shown in Table 14.2. Outliers are identified by visual inspection of the plots and by listing of residuals based on a least-squares regression analysis where a linear relationship exists.

TABLE 14.2. PAIRS OF VARIABLES USED TO CHECK FOR RANDOM AND SYSTEMATIC ERRORS

ANC	vs.	Calcium
		Specific conductance
		Magnesium
		Silica
		pH (Mobile processing lab)
Aluminum (total)	vs.	Ammonium
		Turbidity
		True color
Calcium	vs.	Specific conductance
		Fluoride (total dissolved)
		Sulfate
		Silica
Chloride	vs.	Specific conductance
		Sodium
Specific conductance	vs.	Fluoride (total dissolved)
		Potassium
		Magnesium
		Sodium
		Silica
		Sulfate
Aluminum (organic ext.)	vs.	Potassium
		Magnesium
		Silica
		Aluminum (total ext.)
Potassium	vs.	Magnesium
Ammonium	vs.	Turbidity
		True color
		BNC
Silica	vs.	Mobile processing lab pH
		Magnesium
Turbidity	vs.	True color
pH (mobile processing lab)	vs.	pH (initial and air equilibrated)
DIC (mobile processing lab)	vs.	DIC (initial and air equilibrated)

Observations are identified as outliers if the absolute value of the standardized residual [(actual-predicted)/residual standard deviation] is generally greater than 3. Because the least-squares analysis can be strongly biased by certain types of outliers, the residuals from resistant line fits, lines fit through the medians of partitions of the data, are examined for DOC, true color, and turbidity (Velleman and Hoaglin, 1981). Other variables are treated by use of an iterative process of linear regression, identification and removal of outliers, and repeated linear regression to identify additional outliers that would not have necessarily been identified had major outliers not been removed first.

14.2.5 Multivariate Analyses - Although examination of scatter plots is an important and necessary step for evaluating possible errors in the data, bivariate analyses must be limited to those variables that have obvious associations. The magnitude of the data set precludes examination of all possible distributions and bivariate plots. For example, the number of bivariate plots required for all combinations of the analytical variables exceeds 4,600. Although many of these combinations of variables are of no interest, many combinations remain. Clearly, this is not a practical or efficient method for examining all the data.

An alternative method of examining data for systematic and random errors is through multivariate analysis in which several variables are examined simultaneously. Because theoretical relationships are expected to exist among certain chemical variables, it is useful to examine these sets of variables as groups (Table 14.3).

Two primary multivariate techniques are used to identify outliers: cluster analysis and principal component analysis (PCA). Cluster analysis is a classification technique for identifying similarities (or, conversely, dissimilarities) among observations. Each observation is compared to other observations in the set and is assigned to a group or cluster using a measure of similarity.

The primary clustering technique used in the validation process is the FASTCLUS procedure in SAS (SAS Institute, 1982). This method is a nonhierarchical divisive method that is sensitive to outliers. A less formal clustering technique also used for selected samples is the Trilinear Diagram (Hem, 1970). The Trilinear Diagram is useful for examination of possible errors associated with the major cations and anions. The other clustering techniques are used for related sets of variables such as those shown in Table 14.3.

Principal component analysis is a technique that also is commonly used to reduce large data matrices into manageable dimensions. New variables called principal components are formed from linear combinations of the original variables such that the first principal component reflects

TABLE 14.3. RELATED GROUPS OF VARIABLES USED IN MULTIVARIATE ANALYSES

Group	Variables
1.	Major anions and cations
2.	pH, ANC, DOC, true color
3.	Turbidity, true color
4.	Nitrate, phosphorus, ammonium, turbidity
5.	Anion deficit, DOC, true color
6.	pH; total extractable, organic extractable, and total aluminum; fluoride; DOC
7.	Silica, major cations
8.	Iron, manganese, total extractable and organic extractable aluminum, DOC
9.	ANC, DIC, pH
10.	pH, sulfate, DOC

most of the variance or dispersion in the data. Each successive principal component explains less variance, and examination of the first several components is generally sufficient to describe the data. If the original data are approximately normally distributed, the resulting principal components are also approximately normal. Thus, a plot of any two components typically results in an elliptical cluster with outliers displaced from the ellipse.

Where appropriate, least-squares multiple linear regression techniques also are used to identify observations with high absolute values of the standardized residual.

14.3 Detection of Systematic Error

Methods for evaluating systematic error are less exploratory because they require a source of external comparison. Here the tests are similar to comparison with standards (such as audits or split samples), with one major difference. The external references consist of data sets obtained from other investigators and cannot be viewed as "standards." Hence, a difference between data from NSS and another data source does not necessarily imply that the NSS data are in error. However, comparisons with external data sources serve as aids for evaluating the quality of the data by bringing attention to data that may require additional scrutiny. Clearly, existence of systematic differences between the NSS data and several external data sources would be cause for careful reevaluation of the data in question. Two types of systematic errors are investigated in the NSS data base: a constant additive effect (resulting in a nonzero intercept) and an effect that is dependent on the magnitude of the variable being measured (resulting in a slope $\neq 1$ or nonlinearity in the relationship).

14.4 Treatment of Outliers and Systematic Differences

Data identified as outliers through the procedures described above may be acceptable when evaluated in the context of other variables or when considering limitations of the methods used in NSWS. Therefore, before the original data sources are rechecked, the outliers and systematic differences identified in the validating process are reviewed for plausibility by the staff at ERL-C. Data that remain suspect following screening by staff scientists are sent to the appropriate organization for reexamination.

Outliers and systematic differences for all chemical variables are checked against reported values by staff at EMSL-LV; site location and watershed-related variables are reviewed by the Geographic Research Team at ERL-C; and remaining variables are checked by staff at ORNL. When the data are rechecked for suspect values that were identified during validation of the chemical variables, the following possible conditions may be revealed. These conditions may require the associated response listed:

	Condition	Response
(1)	Suspect value in data set number 2 (verified data set) is found to be a transcription or transposition error.	Correct value is placed in data set number 3 (validated data set).
(2)	Suspect value in data set number 2 agrees with reported value, and value was flagged in verification.	Value is flagged in data set number 3.
(3)	Suspect value in data set number 2 agrees with reported value, but value was not flagged in verification.	Value may be flagged in data set number 3 depending on evidence for possible error.

Values flagged in data set number 2 but not identified as aberrant in data validation remain unchanged and flagged except in cases where the flag is not required for interpretation of the data; in these cases, the flag is removed. The protocol for resolution of outliers for the non-chemical variables is similar, with the exception that response (2) is omitted.

Resolution of systematic differences between NSS and external reference data involves reexamination of the methods used to collect the NSS data. The effort involved in evaluating systematic differences depends on the evidence available to suggest that a bias may exist in the NSS data and the variable under consideration.

In most cases, sufficient information to perform an appropriate correction for bias in the NSS data is not likely to be available. However, the identification of a possible bias is provided to assist the user in interpreting such data. The process of validation is summarized in Figure 14.1.

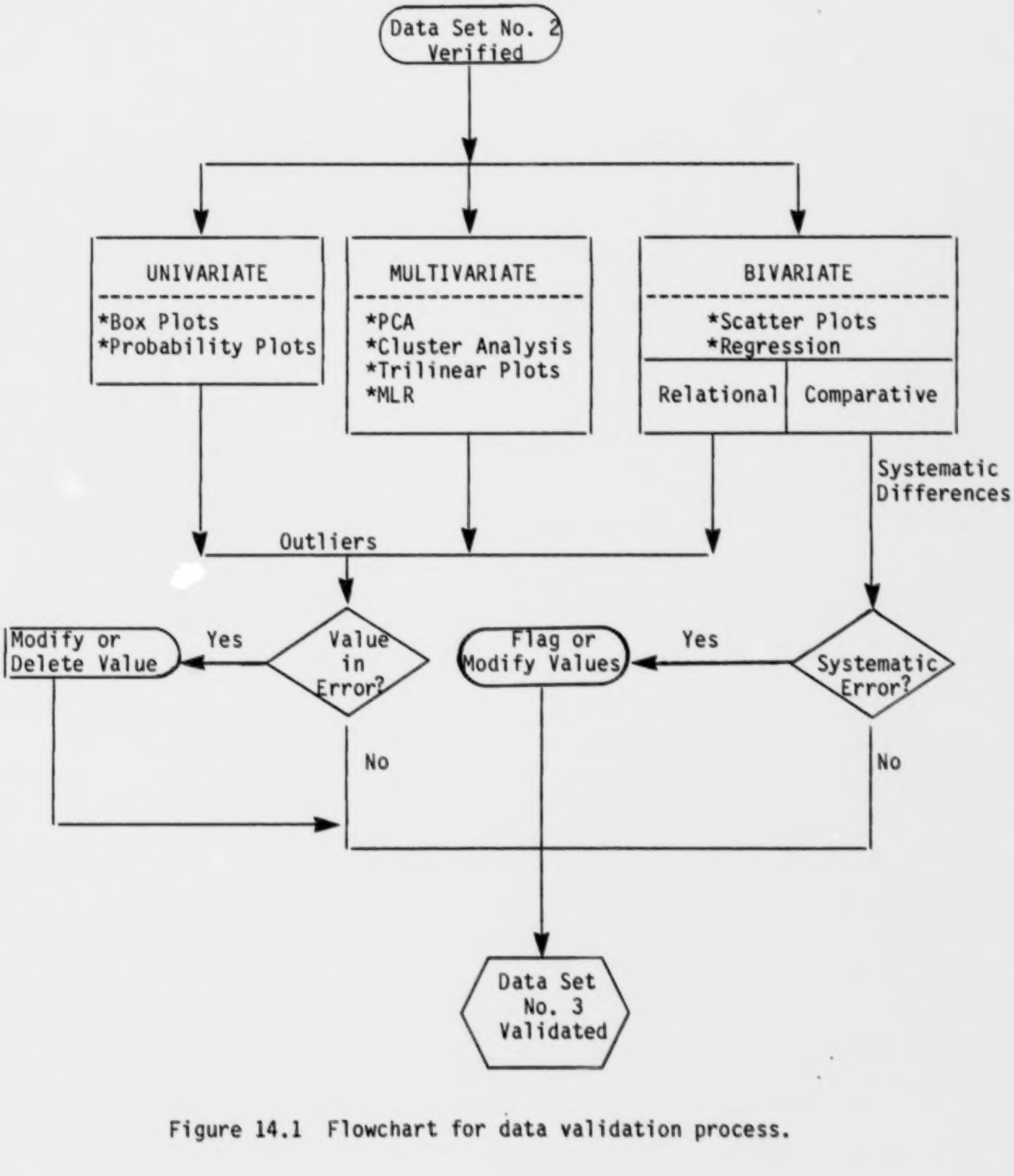

Data Set No. 2 Verified
UNIVARIATE
*Box Plots
*Probability Plots
MULTIVARIATE
*PCA
*Cluster Analysis
*Trilinear Plots
*MLR
BIVARIATE
*Scatter Plots
*Regression
Relational
Comparative
Systematic Differences
Outliers
Value in Error?
Yes
Modify or Delete Value
No
Flag or Modify Values
Yes
Systematic Error?
No
Data Set No. 3 Validated

Figure 14.1 Flowchart for data validation process.

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APPENDIX A

DATA FORMS FOR REPORTING ANALYTICAL RESULTS

NATIONAL SURFACE WATER SURVEY
FORM 11[a]

Page 1 of 2

SUMMARY OF SAMPLE RESULTS

LAB NAME ____________________ **BATCH ID** __________ **LAB MANAGER'S SIGNATURE** ____________________

SAM-PLE ID:	ALIQUOT ID											
	1						2	3				
	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Total Extr. Al mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F^- mg/L
01												
02												
03												
04												
05												
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40												

Note: Approved data qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

NATIONAL SURFACE WATER SURVEY
FORM 11[a]

SUMMARY OF SAMPLE RESULTS

LAB NAME ______________ BATCH ID __________ LAB MANAGER'S SIGNATURE ______________

	ALIQUOT ID											
	4		5								6	7
			Measured									
SAM-PLE ID:	DOC mg/L	NH_4^+ mg/L	Eq. pH	Alk Init. pH	Acy Init. pH	ANC µeq/L	BNC µeq/L	Spec. Cond. µS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total Dissolved P mg/L	Total Al mg/L
01												
02												
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Note: Approved data qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For The Phase I - Pilot Survey, the form includes a column for aliquot 8.

Page 1 of 1

NATIONAL SURFACE WATER SURVEY
Form 13

ANC AND BNC RESULTS

Lab Name____________________ Batch ID________________ Sample ID______________
Lab Manager's Signature________________________ Analyst________________________

RESULTS

[ANC] = ____________________ μeq/L INITIAL SAMPLE VOLUME ________________ mL
[BNC] = ____________________ μeq/L BLANK ANC __________________________ μeq/L

DATA

C_A = ____________________ eq/L DATE STANDARDIZED ____________________
C_B = ____________________ eq/L DATE STANDARDIZED ____________________

ACID TITRATION

VOLUME HCl (mL)	MEASURED pH'	CALCULATED pH
0.00		
0.00 (with KCl)		

BASE TITRATION

VOLUME NaOH (mL)	MEASURED pH'	CALCULATED pH
0.00		
0.00 (with KCl)		

NATIONAL SURFACE WATER SURVEY
Form 14[a]

Page 1 of 1

QC DATA FOR ANC
AND BNC ANALYSES

LAB NAME ______________________ BATCH ID __________

LAB MANAGER'S SIGNATURE ______________________________

SAMPLE ID	ANC µeq/L	BNC µeq/L	CALCULATED ANC		%D[c]
			RESULT	DIFFERENCE[b]	
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
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39					
40					

[a] Form not required in data package but recommended for internal QC requirements.
[b] Difference = Calculated ANC-Measured ANC
[c] Refer to methods manual

NATIONAL SURFACE WATER SURVEY
Form 15[a]

Page 1 of 1

SPECIFIC CONDUCTANCE

LAB NAME ____________________ BATCH ID ______________ LAB MANAGER'S SIGNATURE ____________________

Sample ID	SPECIFIC CONDUCTANCE (µS/cm)			CALCULATED SPECIFIC CONDUCTANCE FOR EACH ION µS/cm											
	Calculated	Measured	%CD[b]	HCO_3^-	Ca^{+2}	CO_3^{-2}	Cl^-	Mg^{+2}	NO_3^-	K^+	Na^+	SO_4^{-2}	NH_4^+	H^+	OH^-
01															
02															
03															
04															
05															
06															
07															
08															
09															
10															
11															
12															
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36															
37															
38															
39															
40															
Specific Conductance Factors of Ions [(µS/cm at 25°C) per mg/L]				0.715	2.60	2.82	2.14	3.82	1.15	1.84	2.13	1.54	4.13	3.5×10^5 (per mole/L)	1.92×10^5 (per mole/L)

Note: Reanalysis criteria are given in Table 9.5 of the QA plan.

[a] Form not required in data package but recommended for internal QC requirements.

[b] $$\%CD = \frac{\text{Calculated Specific Conductance + Measured Specific Conductance}}{\text{Measured Specific Conductance}} \times 100$$

NATIONAL SURFACE WATER SURVEY
Form 16[a]

Page 1 of 1

ANION-CATION BALANCE CALCULATION

LAB NAME ____________________ BATCH ID ________ LAB MANAGER'S SIGNATURE ____________

		Ions - (μeq/L)										
Sample ID	% Ion Difference[b]	Ca^{+2}	Cl^-	Mg^{+2}	NO_3^-	K^+	Na^+	SO_4^{-2}	F^-	NH_4^+	ANC	H^+[c]
01												
02												
03												
04												
05												
06												
07												
08												
09												
10												
11												
12												
13												
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37												
38												
39												
40												
Factors to Convert mg/L to μeq/L		49.9	28.2	82.3	16.1	25.6	43.5	20.8	52.6	55.4	----	----

Note: Reanalysis criteria are given in Table 9.5 of the QA plan.

[a] Form not required in data package but recommended for internal QC requirements.

[b] $\% \text{ Ion Difference } (\%ID) = \frac{ANC + \Sigma \text{ Anions} - \Sigma \text{ Cations (except } H^+)}{ANC + \Sigma \text{ Anions} + \Sigma \text{ Cation} + 2[H^+]} \times 100$

[c] $[H^+] = (10^{-pH}) \times 10^6$

NATIONAL SURFACE WATER SURVEY
Form 17

Page 1 of 1

IC RESOLUTION TEST

LAB NAME ______________________

BATCH ID ______________________

LAB MANAGER'S SIGNATURE ______________________

IC Resolution Test

IC Make and Model: ______________________

Date: ______________

Concentration: SO_4^{2-} ______________ µg/mL, NO_3^- __________ µg/mL

Column Back Pressure (at max. of stroke): ______________ psi

Flow Rate: ____________ mL/min

Column Model: ________________ Date of Purchase: ______________

Column Manufacturer: ______________________

Column Serial No: ______________________

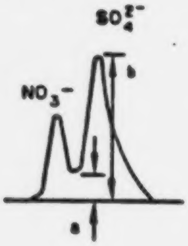
Is precolumn in system ___ Yes ___ No

(a) ________ cm (b) ________ cm

Percentage Resolution: 100 x (1-a/b) ________________

The resolution must be greater than 60%

Test Chromatogram:



NATIONAL SURFACE WATER SURVEY
Form 18[a]

Page 1 of 1

DETECTION LIMITS

LAB NAME ______________________ BATCH ID ________________

LAB MANAGER'S SIGNATURE ______________________________

Parameter	Units	Required Detection Limit	Instrumental Detection Limit[b]	Date Determined (DD MMM YY)
Ca	mg/L	0.01		
Mg	mg/L	0.01		
K	mg/L	0.01		
Na	mg/L	0.01		
Mn	mg/L	0.01		
Fe	mg/L	0.01		
Al, Total Extractable	mg/L	0.005		
Cl^-	mg/L	0.01		
SO_4^{2-}	mg/L	0.05		
NO_3^-	mg/L	0.005		
SiO_2	mg/L	0.05		
F^-, Total Dissolved	mg/L	0.005		
NH_4^+	mg/L	0.01		
DOC	mg/L	0.1		
Specific Conductance	µS/cm	c		
DIC	mg/L	0.05		
P, Total Dissolved	mg/L	0.002		
Al, Total	mg/L	0.005		

Note 1: Report with four significant figures or down to IDL

Note 2: Indicate the instrument for which the IDL applies with an "F" (for Furnace AA), a "P" (for ICP) or an "L" (for Flame AA) after the IDL value.

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

[b] To be calculated as required in Section 9.6 of the QA plan and filled out by the analytical laboratory.

[c] Report the $\bar{X}$, which must not exceed 0.9 µS/cm, of six (6) nonconsecutive blanks.

NATIONAL SURFACE WATER SURVEY
FORM 19[a]

Page 1 of 2

SAMPLE HOLDING TIME SUMMARY

LAB NAME ____________ BATCH ID ________ LAB MANAGER'S SIGNATURE ____________

DATE SAMPLED[b] ____________ DATE RECEIVED[b] ____________

Parameter	Ca	Mg	K	Na	Mn	Fe	Total Extr. Al	Cl^-	SO_4^{2-}	NO_3^-	SiO_2	ISE Total F^-
Holding Time	28	28	28	28	28	28	7	28	28	7	28	28
Holding Time Plus Date Processed												
Sample ID:				Date[b]				Analyzed[c]				
01												
02												
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40												

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form included a column for aliquot 8.

[b] Report these dates as Julian dates (i.e., March 26, 1984 = 4086).

[c] If parameter was reanalyzed because of QA problems, report the last date analyzed.

NATIONAL SURFACE WATER SURVEY
FORM 19[a]

Page 2 of 2

SAMPLE HOLDING TIME SUMMARY

LAB NAME ____________________ BATCH ID __________ LAB MANAGER'S SIGNATURE __________________________

DATE SAMPLED[b] ________________ DATE RECEIVED[b] ______________

Parameter	DOC	NH_4^+	Eq. pH	ANC	BNC	Specific Conductance	Eq. DIC	Init. DIC	Total Dissolved P	Total Al
Holding Time	14	28	14	14	14	14	14	14	28	28
Holding Time Plus Date Processed										
Sample ID:			Date[b]			Analyzed[c]				
01										
02										
03										
04										
05										
06										
07										
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40										

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

[b] Report these dates as Julian dates (i.e., March 26, 1984 = 4086).

[c] If parameter was reanalyzed because of QA problems, report the last date analyzed.

NATIONAL SURFACE WATER SURVEY
FORM 20[a]

Page 1 of 2

BLANKS AND QCCS

LAB NAME ____________________ BATCH ID __________ LAB MANAGER'S SIGNATURE ____________________

	ALIQUOT ID											
	1						2	3				
Parameter	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Total Extr.Al mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F^- mg/L
Calibration Blank												
Reagent Blank	N	N	N	N	N	N	N	N	N	N		N
DL QCCS Theoretical												N
DL QCCS Measured												N
Low QCCS True Value												
Low QCCS Upper Control Limit												
Low QCCS Lower Control Limit												
Initial												
Continuing												
Continuing												
Continuing												
Continuing												
Continuing												
Final												
High QCCS True Value												
High QCCS Upper Control Limit												
High QCCS Lower Control Limit												
Initial												
Continuing												
Continuing												
Continuing												
Continuing												
Continuing												
Final												

Note: Approved data qualifiers and instruction for their use are listed in Table 9.8 of the QA plan.

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

NATIONAL SURFACE WATER SURVEY
FORM 20[a]

Page 2 of 2

BLANKS AND QCCS

LAB NAME __________ BATCH ID __________ LAB MANAGER'S SIGNATURE __________

	ALIQUOT ID									
	4		5						6	7
			Measured							
Parameter	DOC mg/L	NH_4^+ mg/L	Eq pH	ANC pH	BNC pH	Spec. Cond. µS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total Dissolved P mg/L	Total Al mg/L
Calibration Blank			N	N	N					
Reagent Blank	N	N	N	N	N	N	N	N	N	
DL theoretical			N	N	N	N				
QCCS measured			N	N	N	N				
Low QCCS True Value										
Low QCCS Upper Control Limit										
Low QCCS Lower Control Limit										
Initial										
Continuing										
Continuing										
Continuing										
Continuing										
Continuing										
Final										
High QCCS True Value										
High QCCS Upper Control Limit										
High QCCS Lower Control Limit										
Initial										
Continuing										
Continuing										
Continuing										
Continuing										
Continuing										
Final										

Note: Approved data qualifiers and instruction for their use are listed in Table 9.8 of the QA plan.

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

NATIONAL SURFACE WATER SURVEY
FORM 21[a,b]

Page 1 of 2

DILUTION FACTORS

LAB NAME ____________________ BATCH ID __________ LAB MANAGER'S SIGNATURE ____________________

SAM-PLE ID:	ALIQUOT ID											
	1						2	3				
	Ca	Mg	K	Na	Mn	Fe	Total Extr. Al	Cl^-	SO_4^{2-}	NO_3^-	SiO_2	ISE Total F^-
01												
02												
03												
04												
05												
06												
07												
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39												
40												

Note: Indicate samples analyzed on higher concentration range by using a check mark for each parameter.

[a] Form not required in the data package but recommended for QA purposes.

[b] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

NATIONAL SURFACE WATER SURVEY
FORM 21[a,b]

Page 2 of 2

DILUTION FACTORS

LAB NAME ____________________ BATCH ID __________ LAB MANAGER'S SIGNATURE __________

SAMPLE ID:	ALIQUOT ID											
	4		5								6	7
			Measured									
	DOC	NH_4^+	Eq. pH	Alk Init. pH	Acy Init. pH	ANC	BNC	Cond.	Eq. DIC	Init. DIC	Total Dissolved P	Total Al
01												
02												
03												
04												
05												
06												
07												
08												
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39												
40												

Note: Indicate samples analyzed on higher concentration range by using a check mark for each parameter.

[a] Form not required in the data package but recommended for QA purposes.

[b] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

NATIONAL SURFACE WATER SURVEY
Form 22[a]

Page 1 of 2

DUPLICATES

LAB NAME ____________________ **BATCH ID** __________ **LAB MANAGER'S SIGNATURE** ____________________

	ALIQUOT ID											
	1						2	3				
Parameter	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	Mn mg/L	Fe mg/L	Total Extr.Al mg/L	Cl$^-$ mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	SiO_2 mg/L	ISE Total F$^-$ mg/L
Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												
Second Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												
Third Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD												

Note: Approved Data Qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.

[a] This form is used for tne Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

NATIONAL SURFACE WATER SURVEY
Form 22[a]

Page 2 of 2

DUPLICATES

LAB NAME ______________ BATCH ID __________ LAB MANAGER'S SIGNATURE ______________

	ALIQUOT ID											
	4		5								6	7
			Measured									
Parameter	DOC mg/L	NH_4^+ mg/L	Eq. pH	Alk Initial pH	Acy Initial pH	ANC µeq/L	BNC µeq/L	Spec. Cond. µS/cm	Eq. DIC mg/L	Init. DIC mg/L	Total Dissolved P mg/L	Total Al mg/L
Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD[b]												
Second Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD[b]												
Third Duplicate Sample ID												
Sample Result												
Duplicate Result												
% RSD[b]												

Note: Approved Data Qualifiers and instructions for their use are listed in Table 9.8 of the QA plan.

[a] This form is used for the Mid-Atlantic Phase I Survey, the Southeast Screening Survey, and the Episodes Pilot Survey. For the Phase I - Pilot Survey, the form includes a column for aliquot 8.

[b] Report the absolute difference instead of %RSD for pH determinations.

APPENDIX B

FIELD SAMPLING AND MOBILE PROCESSING LABORATORY

ON-SITE EVALUATION QUESTIONNAIRE

GENERAL (Page 1 of 1)

Questionnaire Completion Date ____________

Field Base ______________________________

Location ______________________________

Mobile Processing Laboratory Supervisor ______________________________

Questionnaire Completed By (If more than one auditor, indicate sections completed by each auditor.)

____

____

____

MOBILE PROCESSING LABORATORY PERSONNEL (Page 1 of 1)

Position	Name	Academic Training*	Special Training*	Years Experience**
Mobile Processing Laboratory Coordinator				
Mobile Processing Laboratory Supervisor				
Analyst				
Analyst				
Analyst				

*List highest degree obtained and specialty. Also list years toward a degree.

**List only experience directly relevant to task to be performed.

MOBILE PROCESSING LABORATORY - STANDARD OPERATING PROCEDURES (Page 1 of 1)

Item	Yes	No
Is the training manual followed in detail?		
Are copies available to the personnel?		
Are analysis logbooks kept up to date?		
Are all on-site changes in procedures clearly documented and justified in mobile processing laboratory supervisor's logbook and approved by appropriate personnel?		

Comments: ____

MOBILE PROCESSING LABORATORY FACILITIES (Page 1 of 1)

Item	Yes	No	Comment
Is the laboratory kept clean and organized?			
Are the refrigerator and freezer temperatures monitored on a daily basis and recorded in a logbook?			
Are waste disposal containers available and clearly labeled, and is waste disposed of properly?			
Are chemicals stored properly?			
Is balance calibration checked daily and recorded in a logbook?			
Is water supply purity monitored daily and recorded in a logbook?			

General Comments: ____________________

MOBILE PROCESSING LABORATORY EQUIPMENT (Page 1 of 7)

Color Test Kits

Item	Yes	No	Comment
Is manufacturer's operating manual readily available?			
Is kit cleaned and stored properly?			
Are viewing tubes kept clean?			
Is logbook kept up to date and signed daily?			
Is centrifuge maintained and kept clean?			

Comments: ______________________________

MOBILE PROCESSING LABORATORY EQUIPMENT (Page 2 of 7)

Nephelometer

Item	Yes	No	Comment
Is manufacturer's operating manual available?			
Is instrument kept clean?			
Are cuvettes kept clean and scratch-free?			
Is logbook kept up to date and signed daily?			
Is calibration checked before and after every eight samples?			
Are standards kept refrigerated when not in use?			

Comments: ______

MOBILE PROCESSING LABORATORY EQUIPMENT (Page 3 of 7)

Carbon Analyzer

Item	Yes	No	Comment
Is manufacturer's operating manual available?			
Is instrument kept clean?			
Is the injection valve flushed with deionized water daily after use?			
Is logbook kept up to date and signed daily?			
Is IR analyzer power left on at all times?			
Is standard stock solution prepared biweekly, and is QC stock solution prepared weekly; are they stored at 4°C?			
Are working standards prepared daily?			
Is exposure of samples and standards to the atmosphere minimized?			
Is required QC followed?			
Are pump tubes checked for wear and replaced on a regular basis (about every 2 weeks)?			
Are syringes and glassware cleaned properly after use?			
Are CO_2 and moisture scrubbers on standard bottles replaced when exhausted?			
Is tin scrubber in IR analyzer checked daily and refilled when necessary?			

Comments: ____________________

____

MOBILE PROCESSING LABORATORY EQUIPMENT (Page 4 of 7)

pH Apparatus

Item	Yes	No	Comment
Are meter and electrode operating manuals available?			
Is logbook kept up to date and signed daily?			
Is pH QC sample prepared daily?			
Is electrode stored in 3M KCl?			
Is required QC followed?			
Are electrodes checked and filled (if necessary) prior to use?			
Are sample chambers cleaned after use?			
Are buffers capped tightly after use?			

Comments:

MOBILE PROCESSING LABORATORY EQUIPMENT (Page 5 of 7)

Filtration and Preservation Apparatus

Item	Yes	No	Comment
Is hood kept neat and clean?			
Is contamination evident?			
Is hood sealed when not in use?			
Is filtration apparatus kept ultraclean as specified?			
Are precautions taken to prevent contamination of filtrators, filter funnels, filters, sample bottles, and reagents?			
Is a water trap used with the vacuum pump?			
Are micropipets kept in an upright position at all times?			
Is the calibration of micropipets checked weekly?			
Are sample aliquots properly labeled?			
Is vacuum maintained at 10 to 12 inches Hg while filtering?			

Comments: ____________________

MOBILE PROCESSING LABORATORY EQUIPMENT (Page 6 of 7)

MIBK Extraction

Item	Yes	No	Comment
Is the centrifuge operating manual available?			
Is the extraction logbook kept up to date and signed daily?			
Is leakage of sample volume ($\geq$ 8.5 mL) noted in the logbook?			
Are reagents (NaOAc and hydroxyquinoline) made fresh daily?			
Is NH_4OH made fresh weekly and is the preparation recorded in the logbook?			
Are pipets calibrated weekly?			
Is the 25 mL of standard measured accurately?			
Is the sample buffered to pH 8?			
Is the buffer/MIBK solution shaken vigorously for 10 seconds?			
Is disposal of solid and liquid wastes conducted properly?			

Comments: ____________________

MOBILE PROCESSING LABORATORY EQUIPMENT (Page 7 of 7)

Conductance Meter and Cell

Item	Yes	No	Comment
Is manufacturer's operating manual available?			
Is instrument kept clean?			
Is logbook kept up to date and signed daily?			
Is standard stock solution prepared biweekly, and is QC stock solution prepared weekly; are solutions stored at 4°C?			
Are working standards prepared daily?			
Is exposure of samples and standards to the atmosphere minimized?			
Is required QC followed?			
Are syringes and glassware cleaned properly after use?			

Comments: ____________________

SAMPLE PROCESSING (Page 1 of 1)

Item	Yes	No	Comment
Are all station documents kept in an orderly fashion?			
Are all forms completed as required and signed by supervisor?			
Is lab audit notebook kept up to date (labels inserted, etc.)?			
Are audit samples assigned different ID numbers from day to day?			
Are samples kept at 4°C when not being used?			
Are coolers containing sample kept shut?			
Are freeze-gel packs kept frozen?			
Are samples properly packed for shipping (sealed, cooled to 4°C, individually wrapped, etc.)?			
Are two copies of the completed shipping form included with each batch of samples?			

Comments: ______________________________

____

FIELD PERSONNEL (Page 1 of 1)

Position	Name	Agency	Academic Training*	Special Training*	Years Experience**
A. Base Coordinator					
B. Logistics Coordinator					
C. Team A 1. 2.					
D. Team B 1. 2.					
E. Team C 1. 2.					
F. Team D 1. 2.					
G. Team E 1. 2.					

*List highest degree obtained and specialty. Also list years toward a degree.
**List only experience directly relevant to task to be performed.

FIELD BASE FACILITIES (Page 1 of 1)

Item	Yes	No	Comment
Has adequate space been provided for predeparture activities?			
Are facilities clean and organized?			
Is equipment clean and organized?			

FIELD SAMPLING-PREPARATION (Page 1 of 1)

Item	Yes	No	Comment
Are checklists followed for loading equipment?			
Was sampling ever aborted because of forgotten items?			
Is equipment organized and easily accessible on sampling craft/vehicle?			
Is equipment stored properly to prevent injury or damage during transport?			
Are adequate plans for the excursion made and understood by personnel?			
Does the field base coordinator know where all teams are at any given time?			
Are all meters properly calibrated or checked for calibration?			
Is calibration information completely and correctly recorded?			
Has an itinerary form been filled out completely?			

FIELD SAMPLING-EN ROUTE (Page 1 of 1)

Item	Yes	No	Comment
Are the maps adequate?			
Are there problems locating streams?			
Are the Stream Data Forms understood and correctly filled out?			

FIELD SAMPLING-ON SITE (Page 1 of 1)

Item	Yes	No	Comment
Are procedures clear and easily followed?			
Is required QC followed?			
Are required safety procedures followed?			
Are adequate volumes of sample being taken?			
Are rinse procedures followed carefully?			
Are samples stored correctly?			
Are all forms filled out correctly?			

APPENDIX C

ANALYTICAL LABORATORY ON-SITE EVALUATION QUESTIONNAIRE

GENERAL (Page 1 of 2)

Questionnaire Completion Date ____________

Laboratory: ____

____

Street Address: ____

____

Mailing Address (if different from above): ____________________

____

City: ____

State: ______________________________ Zip: ____________

Laboratory Telephone Number: Area Code: ______ No.: ____________

Laboratory Director: ____

Quality Assurance Officer: ____
(Quality Control Chemist)

Type of Evaluation: ____

Contract Number: ____

Contract Title: ____

____

GENERAL (Page 2 of 2)

Personnel Contacted:

Name	Title

Laboratory Evaluation Team:

Name	Title

ORGANIZATION AND PERSONNEL (Page 1 of 3)

LABORATORY ORGANIZATIONAL CHART

ORGANIZATION AND PERSONNEL (Page 2 of 3)

Analytical Laboratory Personnel

Position	Name	Academic Training*	Special Training	Years Experience**

*List highest degree obtained and specialty. Also list years toward a degree.
**List only experience directly relevant to task to be performed.

ORGANIZATION AND PERSONNEL (Page 3 of 3)

Item	Yes	No	Comment
Do personnel assigned to this project have the appropriate educational background to successfully accomplish the objectives of the program?			
Do personnel assigned to this project have the appropriate level and type of experience to successfully accomplish the objectives of this program?			
Is the organization adequately staffed to meet project commitments in a timely manner?			
Does the QA officer report to senior management levels?			
Was the QA manager available during the evaluation?			
Was the QA officer available during the evaluation?			

LABORATORY MANAGER (Page 1 of 1)

Item	Yes	No	Comment
Does the laboratory manager have his/her own copy of the standard operating procedures?			
Does the laboratory manager have his/her own copy of the instrument performance data?			
Does the laboratory manager have his/her own copy of the latest monthly QC plots?			
Is the laboratory manager aware of the most recent control limits?			
Does the laboratory manager review the following before reporting data: a. The data?			
b. The QC data sheet with analyst's notes?			
c. The QC chemist's blind audit data report?			
d. The calculated vs. measured sample specific conductance?			

STANDARD OPERATING PROCEDURES (SOP) (Page 1 of 1)

Item	Yes	No	Comment
Has SOP Manual been written?			
Is the SOP Manual followed in detail?			
Does it contain all QC steps practiced?			
Does each analyst have a copy at his/her disposal?			
Are plots of instrumental accuracy and precision available for every analysis?			
Are detection limit data tabulated for each analysis?			

LABORATORY FACILITIES (Page 1 of 4)

When touring the facilities, special attention should be given to: (a) the overall appearance of organization and neatness, (b) the proper maintenance of facilities and instrumentation, and (c) the general adequacy of the facilites to accomplish the required work.

Item	Yes	No	Comment
Does the laboratory appear to have adequate workspace (12 sq. feet, 6 linear feet of unencumbered bench space per analyst)?			
Does the laboratory have a source of distilled/demineralized water?			
Is the specific conductance of distilled/demineralized water routinely checked and recorded?			
Is the analytical balance located away from drafts and areas subject to rapid temperature changes?			
Has the balance been calibrated in the past year by a certified technician?			
Is the balance checked with a class S standard before each use, and is the check recorded in a logbook?			
Are exhaust hoods provided to allow efficient work with volatile materials?			
Is the laboratory clean and organized?			

LABORATORY FACILITIES (Page 2 of 4)

Item	Yes	No	Comment
Are contamination-free work areas provided for the handling of toxic materials?			
Are adequate facilities provided for separate storage of samples, extracts, and standards, including cold storage?			
Is the temperature of the cold storage units recorded daily in logbooks?			
Are chemical waste disposal policies/procedures adequate?			
Are contamination-free areas provided for trace-level analytical work?			
Can the laboratory supervisor document that water free of trace contaminants is available for preparing standards and blanks?			
Do adequate procedures exist for disposal of waste liquids from the ICP and AA spectrometers?			
Is the laboratory secure?			
Are all chemicals dated on receipt and thrown away when shelf life is exceeded?			
Are all samples stored in the refrigerator between analyses?			

LABORATORY FACILITIES (Page 3 of 4)

Item	Available		Comments (where applicable, cite system, QC check, adequacy of space)
	Yes	No	
Filter room or desiccator (either is acceptable) maintained at 15° to 35°C and 50% relative humidity			
Gas			
Lighting			
Compressed air			
Vacuum system			
Electrical services			
Hot and cold water			
Laboratory sink			
Ventilation system			
Hood space			
Cabinet space			
Storage space (cite sq. ft.)			
Shared space			

LABORATORY FACILITIES (page 4 of 4)

COMMENTS ON LABORATORY FACILITIES

EQUIPMENT-GENERAL (Page 1 of 1)

Item	Equipment			Condition/age			% of Time Used in Survey
	# of Units	Make	Model	Good	Fair	Poor	
Balance, analytical							
NBS-calibrated thermometer							
Desiccator							
Balance, top loader							
Class "S" weights							
Balance table							
Distilled water or deionized water - to meet Type I Reagent Grade specifications							
Glassware							
Drying oven							
Hot plates							

ICPES/AAS (Page 1 of 4)

Item	Manufacturer	Model	Installation Date
ICP			
Flame AAS			
Flame AAS			
Graphite Furnace AAS			
Data System			
Data System			

Comments on ICP/AAS Instrumentation: ______

ICPES/AAS (Page 2 of 4)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

ICPES/AAS (Page 3 of 4)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ______________			
Are all solutions properly labeled?			
Is the instrument properly vented?			
Is the interference correction automatically performed?			
Are dilute calibration standards prepared fresh weekly? Source ______________			

ICPES/AAS (Page 4 of 4)

Item	Yes	No	Comment
Is the QC check sample prepared from an independent stock? Source ______________			
Is the instrument allowed to warm up at least 15 minutes with the flame on before the final wavelength adjustment is made?			
Is the calibration curve at least a five-point curve?			
Is the first calibration curve of the day checked for detection limit and linearity?			
Are the matrix spike data calculated and plotted immediately after determination?			
Is each new calibration curve checked to see that the change in instrumental response is less than 5%?			
Are the following control samples analyzed with each run?			
Blanks			
QC Sample			
Spiked Sample			
Duplicates			
Does the analyst review the QC data sheet prepared by the data clerk before the analyst decides whether or not to release the data for reporting?			

ION CHROMATOGRAPH (Page 1 of 5)

Item	Manufacturer	Model	Installation Date
IC			
IC			
IC			
Autosampler			
Data System			
Precolumn			
Separator Column			
Supressor Column			

Comments:

ION CHROMATOGRAPH (Page 2 of 5)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

ION CHROMATOGRAPH (Page 3 of 5)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with entering the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ______________			
Are all solutions properly labeled?			

ION CHROMATOGRAPH (Page 4 of 5)

Item	Yes	No	Comment
Are dilute calibration standards prepared fresh weekly? Source ______________			
If manual techniques are used, is eluant prepared fresh daily from the same concentrated stock buffer?			
Is the QC check sample prepared from an independent stock? Source ______________			
Is the calibration curve at least a four-point curve for each analytical range?			
Is the first calibration curve of the day checked for detection limit and recovery?			
Are the analyst's spike data calculated and plotted immediately following determination?			
Are the following control samples analyzed with each run? Blanks			
QC Sample			
Spiked Sample			
Duplicates			
Does the analyst review the QC data sheet output by the data clerk and then decide whether or not to release the data for reporting?			
Is the drip tray examined daily for reagent spills, and are spills cleaned up daily?			

ION CHROMATOGRAPH (Page 5 of 5)

Item	Yes	No	Comment
Are pumps oiled once per week?			
Is the anion precolumn cleaned as necessary?			
Is the SO_4^{2-}/NO_3^- resolution checked once per batch and documented?			

ACIDITY AND ALKALINITY (Page 1 of 4)

A. Manual System

Item	Manufacturer	Model	Installation Date
pH Meter			
Electrodes			
Data System			

Titration Apparatus (burets, etc.): ______________________________

____

B. Automated System

Item	Manufacturer	Model	Installation Date
System			
Meter			
Electrodes			

Auto Titration Specifications: ______________________________

____

____

Comments: ______________________________

____

ACIDITY AND ALKALINITY (Page 2 of 4)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are entries in the notebook legible?			

ACIDITY AND ALKALINITY (Page 3 of 4)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printout, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with entering the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ______________			
Are all solutions properly labeled?			
Are burets and micropipets calibrated weekly or more often?			
Is the stock 1.0 and 0.01 N NaOH standardized as required in methods manual?			
Are the correlation coefficients of the data examined to ensure that they are greater than 0.9990?			

ACIDITY AND ALKALINITY (Page 4 of 4)

Item	Yes	No	Comment
Does the analyst review the QC data sheet prepared by the data clerk before the analyst decides whether or not to release the data for reporting?			
Are electrodes stored as recommended by the manufacturer?			
Are electrodes checked and filled, if necessary, before each analysis?			

pH (Page 1 of 4)

Item	Manufacturer	Model	Installation Date
Meter			
Electrodes			

Type of Temperature Compensation ____________________

Standard Gas Supplier ____________________

Standard Gas Specifications ____________________

Comments: ____________________

pH (Page 2 of 4)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

pH (Page 3 of 4)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with entering the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Is the pH meter calibrated before samples are analyzed?			
Is the pH meter calibration checked every batch as required in the methods manual?			
Is the pH electrode QC solution analyzed first and as specified, and are the results plotted immediately after determination?			

pH (Page 4 of 4)

Item	Yes	No	Comment
Does the material used as a QC sample meet specifications? Source of QCCS:			
Are the following control samples analyzed with each run: QCCS			
Duplicate			
Does the analyst review the QC data sheet prepared by the data clerk before the analyst decides whether or not to release the data for reporting?			
Are electrodes stored as recommended by the manufacturer?			
Are electrodes checked and filled, if necessary, before each analysis?			

FLUORIDE ION SELECTIVE ELECTRODE (Page 1 of 3)

Item	Manufacturer	Model	Installation Date
Meter			
Electrodes			

Comments:

FLUORIDE ION SELECTIVE ELECTRODE (Page 2 of 3)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

FLUORIDE ION SELECTIVE ELECTRODE (Page 3 of 3)

Item	Yes	No	Comment
Are entries noting anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with entering the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Is there an electrode dedicated to low-level F^- analysis?			
Is all labware that comes in contact with standards and samples made of plastic?			
Is the temperature regulated?			
Is a multipoint calibration used?			

CARBON ANALYZER (Page 1 of 3)

Make and Model: ____

Specifications: ____

____

Comments: ____

____

____

____

____

____

____

____

____

CARBON ANALYZER (Page 2 of 3)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

CARBON ANALYZER (Page 3 of 3)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with entering the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ______________			
Are all solutions properly labeled?			
Is CO_2-free water used to prepare standards?			
Are precautions taken to prevent CO_2 contamination of samples and standards?			
Is instrument designed to determine both DOC and DIC? If not, what modifications are necessary?			

AUTOMATED ANALYZER (Page 1 of 5)

Item	Manufacturer	Model	Installation Date
Automated Analyzer			
Electrodes			
Data System			

Comments: ____

AUTOMATED ANALYZER (Page 2 of 5)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his own copy of the instrument performance data?			
Does the analyst have his own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

AUTOMATED ANALYZER (Page 3 of 5)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with entering the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ____________			
Are all solutions properly labeled?			
Are dilute calibration standards prepared fresh daily? Source ____________			
Is the QC check sample prepared fresh daily from an independent stock? Source ____________			

AUTOMATED ANALYZER (Page 4 of 5)

Item	Yes	No	Comment
Is the calibration curve at least a five-point curve?			
Is the first calibration curve of the day checked for detection limit(s) and linearity?			
Are the analyst QC sample data calculated and plotted real time?			
Is there an automated analyzer dedicated to each analysis (Total P, NH_4^+ SiO_2)?			
Is each new calibration curve checked to see that the change in instrumental response is less than 5%?			
Are the following control samples analyzed with each run?			
Reagent Blanks			
QC Sample			
Spiked Sample			
Duplicates			
Does the analyst review the QC data sheet prepared by the data clerk and then decide whether or not to release the data for reporting?			
Is the water pumped through all lines daily before and after analysis?			
Are pump tubes changed at least once per three days?			
Is the pump cleaned when the pump tubes are changed?			

AUTOMATED ANALYZER (Page 5 of 5)

Item	Yes	No	Comment
Is soap solution that does not contain phosphorus pumped through all lines once per week?			
Is the flowcell cleaned with a sulfuric acid-potassium dichromate solution once per month?			
Is the pump oiled once every three months? Date of last service __________			
Is the colorimeter mirror assembly and color filter cleaned and the alignment optimized once every three months? Date of last service __________			

SPECIFIC CONDUCTANCE (Page 1 of 3)

Item	Manufacturer	Model	Installation Date
Meter			
Conductance Cell			

Is temperature compensated to 25°C? ____________________

What is the cell constant? ____________________

Comments: ____________________

SPECIFIC CONDUCTANCE (Page 2 of 3)

Item	Yes	No	Comment
Has the instrument been modified in any way?			
Is a permanent service record maintained in a logbook?			
Is service maintenance by contract?			
Is preventive maintenance applied?			
Does the analyst have his/her own copy of the standard operating procedures?			
Are manufacturer's operating manuals readily available to the analyst?			
Is there a calibration protocol available to the analyst?			
Are calibration results kept in a permanent record?			
Does the analyst have his/her own copy of the instrument performance data?			
Does the analyst have his/her own copy of the latest weekly QC plots?			
Is the analyst aware of the most recent control limits?			
Is a permanently bound notebook with preprinted, consecutively numbered pages being used?			
Is the type of work clearly displayed on the notebook?			
Are the entries in the notebook legible?			

SPECIFIC CONDUCTANCE (Page 3 of 3)

Item	Yes	No	Comment
Are anomalies routinely recorded?			
Has the analyst avoided obliterating entries?			
Are inserts (e.g., chromatograms, computer printouts, etc.) permanently affixed in notebook and signed across insert edge and page?			
Has the supervisor of the individual maintaining the notebook personally examined and reviewed the notebook periodically, and signed his/her name therein, together with entering the date and appropriate comments as to whether or not the notebook is being maintained in an appropriate manner?			
Does the analyst have a copy of the most recent list of in-house samples to be analyzed? Date of list ______________			
Are all solutions properly labeled?			

DOCUMENTATION/TRACKING (Page 1 of 1)

Item	Yes	No	Comment
Is a sample custodian designated? If yes, what is the name of the sample custodian? Name ____________________			
Are the sample custodian's procedures and responsibilities documented? If yes, where are they documented?			
Are written Standard Operating Procedures (SOPs) developed for receipt of samples? If yes, where are the SOPs documented (laboratory manual, written instructions, etc.)?			
Are written Standard Operating Procedures (SOPs) developed for compiling and maintaining sample document files? If yes, where are the SOPs documented (laboratory manual, written instructions, etc.)?			
Are samples that require preservation stored in such a way as to maintain their preservation? If yes, how are the samples stored?			
After completion of the analysis, are the samples properly stored for 6 months or until laboratory personnel are told otherwise?			
Are the magnetic tapes stored in a secure area?			

ANALYTICAL METHODOLOGY (Page 1 of 2)

Item	Yes	No	Comment
Are the required methods used?			
Is there any unauthorized deviation from contract methodology?			
Are written analytical procedures provided to the analyst?			
Are reagent-grade or higher purity chemicals used to prepare standards?			
Are fresh analytical standards prepared at a frequency consistent with good QA?			
Are reference materials properly labeled with concentrations, date of preparations, and the identity of the person preparing the sample?			
Is a standard preparation and tracking logbook maintained?			
Do the analysts record bench data in a neat and accurate manner?			
Is the appropriate instrumentation used in accordance with the required protocol(s)?			

ANALYTICAL METHODOLOGY (Page 2 of 2)

COMMENTS ON ANALYTICAL METHODS AND PRACTICES

QUALITY CONTROL (Page 1 of 3)

Item	Yes	No	Comment
Does the laboratory maintain a QC manual?			
Does the manual address the important elements of a QC program, including the following:			
a. Personnel?			
b. Facilities and equipment?			
c. Operation of instruments?			
d. Documentation of procedures?			
e. Procurement and inventory practices?			
f. Preventive maintenance?			
g. Reliability of data?			
h. Data validation?			
i. Feedback and corrective action?			
j. Instrument calibration?			
k. Recordkeeping?			
l. Internal audits?			

QUALITY CONTROL (Page 2 of 3)

Item	Yes	No	Comment
Are QC responsibilities and reporting relationships clearly defined?			
Have standard curves been adequately documented?			
Are laboratory standards traceable?			
Are QC charts maintained for each routine analysis?			
Do QC records show corrective action when analytical results fail to meet QC criteria?			
Do supervisory personnel review the data and QC results?			
Does the QC chemist have his/her own copy of the standard operating procedures?			
Does the QC chemist have his/her own copy of the instrument performance data?			
Does the QC chemist have his/her own copy of the latest QC plots?			
Is the QC chemist aware of the most recent control limits?			
Does the QC chemist prepare a blind audit sample once per week?			
Does the QC chemist routinely review and report blank audit data to the laboratory manager?			

QUALITY CONTROL (Page 3 of 3)

Item	Yes	No	Comment
Does the QC chemist update control limits and obtain new control chart plots once per day of analysis?			
Are all QC data (control charts, regression charts, QC data bases, etc.) up to date and accessible?			
Are minimum detection limits calculated as specified?			
Is QC data sheet information reported to the analyst?			

DATA HANDLING (Page 1 of 2)

Item	Yes	No	Comment
Does the data clerk do a 100% check for accuracy of data input to the computer?			
Are data calculations checked by another person?			
Are data calculations documented?			
Does strip chart reduction by on-line electronic digitizing receive at least 5% manual spot checking?			
Are manually interpreted strip chart data spot-checked after initial entry?			
Do laboratory records include the following information? Sample identification number			
Station identification			
Sample type			
Date sample received in laboratory			
Time, date, and volume of collection			
Date of analysis			
Analyst			
Result of analysis (including raw analytical data)			
Receptor of the analytical data			

DATA HANDLING (Page 2 of 2)

Item	Yes	No	Comment
Does laboratory follow required sample tracking procedures from sample receipt until discard?			
Does the data clerk routinely report QC data sheet information to the analyst?			
Does the data clerk submit QC data sheet information to the lab manager along with the analytical data to be reported?			
Do records indicate corrective action taken?			
Are provisions made for data storage for all raw data, calculations, QC data, and reports?			
Are all data and records retained the required amount of time?			
Are computer printouts and reports routinely spot-checked against laboratory records before data are released?			

SUMMARY (Page 1 of 2)

Item	Yes	No	Comment
Do responses to the evaluation indicate that project and supervisory personnel are aware of QA and its application to the project?			
Do project and supervisory personnel place positive emphasis on QA/QC?			
Have responses with respect to QA/QC aspects of the project been open and direct?			
Has a cooperative attitude been displayed by all project and supervisory personnel?			
Does the organization place the proper emphasis on QA?			
Have any QA/QC deficiencies been discussed before leaving?			
Is the overall QA adequate to accomplish the objectives of the project?			
Have corrective actions recommended during previous evaluations been implemented?			
Are any corrective actions required? If so, list the necessary actions below.			

SUMMARY (Page 2 of 2)

Summary Comments and Corrective Actions

APPENDIX D

NATIONAL STREAM SURVEY
PREAWARD AUDIT SAMPLE SCORING SHEET

NATIONAL STREAM SURVEY
Preaward Audit Sample Scoring Sheet

Laboratory: ____________________ Date: ____________________

Sample Set 1 ____________________ QA/QC ____________________

Sample Set 2 ____________________ Deliverables ____________________

Quantitation: ____________________

Total Score (Maximum = 200 points)

PART I. QUANTITATION

	Points Awarded Sample Set 1 (Low Conc.)	Points Awarded Sample Set 2 (High Conc.)	Total Score
A. Aliquot 1 (Number of parameters within acceptance criteria x 12/6*)			
B. Aliquot 2 (Number of parameters within acceptance criteria x 8/1*)			
C. Aliquot 3 (Number of parameters within acceptance criteria x 14/5*)			
D. Aliquot 4 (Number of parameters within acceptance criteria x 8/2*)			
E. Aliquot 5 (Number of parameters within acceptance criteria x 30/5*)			
F. Aliquot 6 (Number of parameters within acceptance criteria x 4/1*)			
G. Aliquot 7 (Number of parameters within acceptance criteria x 4/1*)			

*Number of parameters present in aliquot. The scoring for pH and DIC is based on the air-equilibrated values.

Laboratory: ______________________ Date: ______________

PART II. QUALITY ASSURANCE

	Possible Points	Points Awarded
A. Calibration/Reagent Blank Analyses:		
1. All parameters at less than 2 x CRDL.	6	
2. One parameter at greater than 2 x CRDL.	4	
3. Two parameters at greater than 2 x CRDL.	2	
4. Three or more parameters at greater than 2 x CRDL.	0	
B. Quality Control Check Sample		
1. All verifications within acceptance criteria.	10	
2. One or more verifications outside acceptance criteria.	0	
C. Duplicate Sample Analyses:		
1. All %RSD values within acceptance criteria.	6	
2. 1-2 outside acceptance criteria.	4	
3. 3-4 outside acceptance criteria.	2	
4. 5 or more outside acceptance criteria.	0	

Laboratory: ______________________________ Date: ________________

PART II. QUALITY ASSURANCE (Continued)

	Possible Points	Points Awarded
D. Anion-Cation Balance Calculation:		
1. Within acceptance criteria.	4	
2. Outside acceptance criteria.	0	
E. Detection Limits:		
1. All instrumental detection limits within acceptance criteria.	4	
2. One or more outside acceptance criteria.	0	

PART III. REPORTING AND DELIVERABLES

	Possible Points
A. Data results submitted in acceptable format on standard forms.	2
B. Quality assurance/quality control data supplied in acceptable format.	1
C. Raw data supplied.	5
D. Tabulated instrument detection limits and associated blank data supplied.	1
E. Validation of results with signature of laboratory manager supplied.	1

APPENDIX E

NATIONAL STREAM SURVEY
VERIFICATION REPORT

1.0 NATIONAL STREAM SURVEY VERIFICATION REPORT

The NSS Verification Report is used as a guideline to evaluate and verify National Stream Survey data.

The verification report is completed for every batch of data by deleting the inappropriate verb of a verb pair (i.e., were/were not, was/was not, etc.) and listing the affected samples and analyses. Those sections which do not apply are crossed out. Explanations of the reasons for flagging the data are necessary.

NSS VERIFICATION REPORT

BATCH NO. ______________________

SAMPLING SITE(S) ______________________

LABORATORY ______________________

TOTAL NO. OF SAMPLES __________

DATE AUDITED ______________________

BY ______________________

DATE REVIEWED ______________________

BY ______________________

DATE VERIFIED (FIRST PASS) __________

DATE VERIFIED (FINAL) __________

DATE TAPE (FIRST PASS) SENT TO ORNL ______________________

DATE VERIFIED TAPE (FINAL) SENT TO ORNL ______________________

I. OUTSTANDING ISSUES - ANALYTICAL LABORATORY

A. The Sample Data Package (was/was not) complete as submitted. The following items that are identified as missing should be resubmitted before verification process can begin.

	Yes	Partial	No	Comments
1. a. Required forms (11, 13, 17, 18, 19, 20, and 22) submitted.				
b. Lab name, batch ID, and lab manager's signature submitted on all forms.				

(continued)

	Yes	Partial	No	Comments
c. Sample ID reported on Forms 13, 21, and 22.				
d. Analyst's signature on Form 13.				
e. Correct units indicated on all forms.				
2. Form 11:				
a. Correct number of samples analyzed and the results for each parameter tabulated.				
b. Correct data qualifiers (see Table 9.8) reported as needed.				
c. Alk. Initial pH and Acy. Initial pH are within 0.1 pH unit.				
d. For all sample data, pH (initial/equilibrated) increases as DIC (initial/equilibrated) decreases and vice versa.				
e. Total extractable aluminum < total aluminum for all samples.				
3. Form 17:				
a. IC Resolution data reported for each batch of analyses.				
4. Form 18:				
a. Instrumental detection limits and associated dates of determination tabulated.				
5. Form 19:				
a. Date sampled, date received, holding time plus date sampled and dates of analyses for the correct number of samples are tabulated.				
b. Date analyzed is less than or equal to the reported holding time plus date processed.				
c. pH measurements are performed on the same day as the DIC analysis for each sample.				
6. Form 20:				
a. Calibration blanks, reagent blanks, correct number of QCCS runs, and DL QCCS reported where required.				
b. If high QCCS true values are reported, the samples analyzed on high range are discussed in the cover letter or reported on Form 21 (Dilution Factors).				
c. QCCS true values are in the midrange of linear dynamic range, otherwise DL QCCS data are used to verify the low end of the dynamic range.				

	Yes	Partial	No	Comments
d. Calibration blank data are indicative of instrument drift (greater than 2X CRDL for positive values or less than [-] CRDL for negative values).				
e. Calibration blank data do not indicate any trends throughout all batches.				
7. Form 21: a. Dilution Factors (if any) are reported for each required parameter.				
8. Form 22: a. Duplicate precision results are reported for each parameter.				
b. Correct standard deviation formula (using n-1) is used to calculate %RSD.				
c. Samples selected for duplicate analysis contained sufficient amounts of analytes (10 times the CRDL if possible) to yield reliable precision.				
d. If %RSD criterion is not met, another sample is selected to be analyzed in duplicate.				
e. Sample results on Form 22 match sample results on Form 11.				
9. Any information pertinent to sample analyses are noted on the cover letter.				

B. The Sample Data Package (was/was not) complete as submitted, but the following sample results should be confirmed by the analytical laboratory:

Sample ID	Form Number	Parameter	Date Requested	Date Confirmed	Reason for Confirmation

C. Sample analysis (was/was not) complete based on data submitted. Reanalysis is recommended for the following samples:

Sample ID	Parameter	Reported Value	Date Requested	Date Submitted	Reason for Reanalysis

II. OUTSTANDING ISSUES - SAMPLE MANAGEMENT OFFICE (SMO)

HOLDING TIME EXCEPTION AND 15 PERCENT QC WITHHOLDING

SAMPLE ID	Parameter	Holding Time Group	Days Exceeding Holding Time	Flagged "HO" (Y, N)	Cause of Exception	Reason for Recommendation of Penalty/Waiver	EMSL-LV QA Recommendation[a]	EPA Approval

[a] P = Penalty
W = Waiver

Date Changes Applied: __________

By: __________

III. NUMERIC AND FLAG MODIFICATIONS (ADDITIONS OR DELETIONS) TO BE MADE TO THE RAW DATA SET

Batch ID	Form No.	Sample ID	Stream ID	Variable Name (Field ID)	Old Flag	New Flag	Old Value	New Value	Date Edited	By	Date Reviewed	By

IV. ANION/CATION BALANCE CHECK

Note: The flagged samples and parameters listed in the following sections must be consistent with the most current computer-generated exceptions.

A. Based on Anion/Cation balance check program, all samples submitted for this batch (were/were not) within criteria. The following samples were listed as exceptions:

Sample ID	Sample Type	Reported % Ion Bal. Diff. (IBD)	Required % Ion Bal. Diff. (IBD)	Explanation

Samples listed above should be flagged appropriately as outlined in the following sections:

1. Contamination (was/was not) indicated in the field or laboratory blanks for the above exceptions. Contamination was apparent in the following samples:

Sample ID	Parameter	Field/Lab Blank Conc.	Explanation

The sample(s) listed above should be flagged using the appropriate sample flag "A2" or "A3."

2. Unmeasured organic protolytes (were/were not) indicated by the Protolyte Analysis Program for the exceptions listed in Section IV-A. The following samples appear to have %IBD outside criteria because of unmeasured organic protolytes:

Sample ID	Reported DOC (mg/L)	Non-titrated Organic Ions	Recalculated %IBD (Organic Ions Included)	Explanation

The samples listed above should be flagged using the sample flag "A4."

3. Analytical Error (was/was not) indicated in measurement of one or more of the anions or cations contributing to the anion/cation balance check calculation. Analytical error was apparent in the following parameters and samples:

Sample ID	Parameter	Reported Conc.	Explanation

The samples listed above should be flagged using the appropriate sample flags "A5," "A6," "A7," or "A8."

4. Other unmeasured anions or cations not considered in %IBD calculation (were/were not) suspected to contribute to anion/cation balance. The following samples were suspected to contain unmeasured anions or cations:

Sample ID	Suspect Unmeasured anion/cation	Reported Conc.	Explanation

The sample(s) listed above should be flagged for the suspect anion or cation using the sample flag "A1."

5. Analytical error (was/was not) indicated in measurement of acid neutralizing capacity (alkalinity) that affects the %IBD calculation. Analytical error was apparent in the following samples:

Sample ID	Reported Value, µeq/L	Recalculated value, µeq/L	Explanation

The sample(s) listed above should be flagged using the sample flag "A9."

V. CONDUCTANCE BALANCE CHECK

A. Based on conductance check program, all samples submitted for this batch (were/were not) within criteria. Using the conductance check program, the following conclusions were made:

1. The Form 11 measured conductance (agreed/disagreed) with the calculated conductance. The following samples had a Form 11 measured conductance (greater/less) than the calculated conductance:

Sample ID	Form 11 Conductance	Calculated Conductance	Calculated Laboratory % CD	Required Maximum %CD	Explanation

2. The mobile processing laboratory (trailer) conductance (agreed/disagreed) with the Form 11 measured conductance. The following samples had a mobile processing laboratory conductance (greater/less) than the Form 11 measured conductance:

Sample ID	Trailer Conductance	Form 11 Measured Conductance	Calculated Trailer % CD	Required Maximum %CD	Explanation

The sample(s) listed above should be flagged using sample flag "F6."

3. The field in situ conductance (agreed/disagreed) with the Form 11 measured conductance. The following samples had a field in situ conductance (greater/less) than the Form 11 measured conductance.

Sample ID	Field In situ Conductance	Form 11 Conductance	Calculated Field % CD	Required Maximum %CD	Explanation

The sample(s) listed above should be flagged using sample flag "FO."

4. Contamination (was/was not) indicated by the field or lab blanks for the above exceptions. Contamination was apparent in the following samples:

Sample ID	Contaminated Parameters	Field/Lab Blank Concentration	Explanation

The sample(s) listed above should be flagged using the appropriate sample flag "C2" or "C3."

5. The % Conductance Difference (%CD) indicates possible analytical error in the analytical laboratory conductance measurement for the following samples:

Sample ID	%CD	Contract Required Max %CD	Explanation

Samples listed above should be flagged using the sample flag "C5."

6. The % Conductance Difference (%CD) indicates analytical error in the trailer and/or field conductance measurements for the following samples:

Sample ID	Trailer %CD	Contract Required Max %CD (Trailer)	Field %CD	Contract Required Max %CD (Field)	Explanation

Samples listed above should be flagged using the sample flags "F0" (field) and/or "F6" (trailer).

7. Based on review of the data, unmeasured organic ions (were/were not) suspected in the samples. The following samples are suspected to contain unmeasured organic ions:

Sample ID	Reported DOC (mg/L)	Explanation

All samples listed above should be flagged unmeasured organic ions using the sample flag "C4."

8. Analytical error (was/was not) indicated in the calculated conductance value. Analytical error was apparent in the following parameters and samples.

Sample ID	Parameter	%CD	Contract Required Max %CD	Explanation

The sample(s) listed above should be flagged using the appropriate sample flags "C1," "C6," "C8," or "C9."

9. Other unmeasured anions or cations not considered in the %CD calculation (were/were not) suspected to contribute to conductance balance. The following samples were suspected to contain unmeasured anions or cations:

Sample ID	Suspect Unmeasured Anion/Cation	Reported Conc.	Explanation

The samples listed above should be flagged using the sample flag "C7."

VI. INTERNAL AND EXTERNAL QA/QC DATA REVIEW

A. All data for the following parameters and samples were not acceptable based on the following:

1. The field blank (did/did not) exceed expected values and (did/did not) contribute greater than 20% to the other samples in the batch (except for other blanks). The contaminated samples follow:

Sample ID	Parameter	% Contribution	Explanation

All samples for the parameters listed above should be flagged using the appropriate flags "B0," "B2," or "B5."

2. The calibration and/or reagent blank (was, was not) greater than 2 X CRDL and (did/did not) contribute greater than 10% to the other samples in the batch. The contaminated samples follow:

Sample ID	Parameter	% Contribution	Explanation

All samples for the parameters listed above should be flagged using the appropriate flags "B1," "B3," "B4."

3. For a routine-field duplicate sample pair with both concentrations greater than 10 times the CRDL, the field duplicate precision (was/was not) within expected criteria. The maximum expected %RSD was exceeded for the following parameters:

Parameter	Reported %RSD	Contract Required Maximum %RSD	Explanation

The parameters listed above should be flagged using the flag "D2."

4. The contract laboratory duplicate precision (was/was not) met. If initial precision was outside criteria, two additional duplicates (were/were not) run as required by the contract.

Parameter	Reported %RSD	Program Calculated %RSD	Contract Required %RSD	Explanation

The parameters listed above should be flagged using the flag "D3."

5. Audit sample data (were/were not) within the expected performance range. The following audit samples were outside of the expected range:

Parameter	Audit Sample Type	Reported Value	Expected Range	Explanation

All samples in the batch for the parameters listed above should be flagged using the appropriate flags "NO" or "N1."

6. Internal Quality Control Check Sample (QCCS) analyses (were/were not) within contractual requirements and the number of runs (were/were not) complete.

Parameter	Reported Value	Required Range	No. of QCCS Runs	No. of QCCS Runs Required	Explanation

All samples in the batch for the parameters listed above should be flagged using the appropriate flags "Q1" or "Q2" or if appropriate "Q3" or "Q4."

7. Detection Limit Quality Control Check Sample (DL QCCS) analyses (were/were not) within 20% of the theoretical concentration and the theoretical concentration of the QCCS (was/was not) 2 to 3 times the CRDL.

Parameter	Reported Value	Required Range	Explanation

All samples listed above should be flagged using the flag "Q5."

8. Instrumental detection limit (did/did not) exceed the CRDL. The following sample values reported at less than 10 times the IDL could be in question:

Sample ID	Parameter	Reported Conc.	Reported IDL	CRDL	Explanation

All samples with concentrations <10 x IDL for the parameters listed above are in question and should be flagged using the flag "L1."

VII. SUMMARY OF FLAGGED DATA

All internal QC data (calibration blanks, reagent blanks, QCCS, duplicate precision) and external QA data (audits, field blanks, and field duplicates) were not within contractual or expected criteria for all the samples and the associated parameters listed below:

(Parameter Flags: B0, B1, B3-B5, D1-D3, N0, N1, Q1-Q5)

(Sample Flags: A0-A8, B2, C0-C9, F0-F6, H0-H1, L1, P0-P7, X0-X4)

Parameter Flags and Parameters: ______________________________

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Sample Flags, Parameters, and Sample IDs: ______________________

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